00039168

Digitized with financial assistance from

H T Parekh
FOUNDATION

An Initiative by
HDFC
WITH YOU, RIGHT THROUGH

on 15 October, 2018

A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. I.

A DICTIONARY OF APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

Assisted by Eminent Contributors

REVISED AND ENLARGED EDITION

IN FIVE VOLUMES

Containing upwards of 6000 Articles, many with Illustrations

VOL. I.	**A-Che**	**50s. net**
VOL. II.	**Chi-Go**	**50s. net**
VOL. III.	**Gr-Oils**	**50s. net**
VOL. IV.	**Oilstone–Soda Nitre**	**50s. net**
VOL. V.	**Sodium-Z**	**50s. net**

LONGMANS, GREEN AND CO.

LONDON, NEW YORK, BOMBAY, CALCUTTA, AND MADRAS

A DICTIONARY

OF

APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

EMERITUS PROFESSOR OF GENERAL CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES OF THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, LONDON; LATE PRINCIPAL OF THE GOVERNMENT LABORATORY, AND A PAST PRESIDENT OF THE CHEMICAL SOCIETY AND OF THE SOCIETY OF CHEMICAL INDUSTRY

39168 ac

ASSISTED BY EMINENT CONTRIBUTORS

IN FIVE VOLUMES

VOL. I.

REVISED AND ENLARGED EDITION

WITH ILLUSTRATIONS

LIBRARY OF THE BOMBAY BRANCH OF THE ROYAL ASIATIC SOCIETY

NEW IMPRESSION

LONGMANS, GREEN, AND CO.
39 PATERNOSTER ROW, LONDON
FOURTH AVENUE & 30TH STREET, NEW YORK
BOMBAY, CALCUTTA, AND MADRAS
1918

All rights reserved

R L
660·3
Tho
39168

00039168

PREFACE

DURING the twenty-two years that have elapsed since the first volume of this work made its appearance, chemistry has advanced at a rate and to an extent altogether unprecedented in its history, or, indeed, in the history of any other science. This extraordinary growth has been accompanied by a no less remarkable increase in the variety and comprehensiveness of its applications to the arts and manufactures. Accordingly, in the attempt to make this reissue reasonably adequate as a presentation of contemporary knowledge, both as regards the science and its applications, it has been found absolutely necessary to enlarge greatly the original scope of the book. All the articles in the former issue have been carefully revised and many have been wholly rewritten. In addition, of course, a large number of new and important subjects have had to be dealt with. The result is that this edition of the Dictionary of Applied Chemistry is practically a new work.

In preparing it the Editor has again been fortunate in securing the co-operation of eminent authorities, not only in the United Kingdom, but also in America, Germany, Switzerland, etc., as writers on subjects with which they are specially qualified to treat. A list of these, with the titles of their contributions, is prefixed to the several volumes in which these contributions appear. Their names and standing are a sufficient guarantee that no pains have been spared to make the work a faithful record of the present relations of chemistry to the arts and manufactures.

The Editor desires to express his acknowledgments to the following Demonstrators, Assistant-Demonstrators, and Assistants in the Chemical Department of the Imperial College of Science and Technology for help in the revision and compilation of the subject-matter of many of the articles: Dr. W. N. Haworth; Dr. H. F. Harwood, M.Sc.; Dr. P. W. Robertson, M.A., M.Sc.; Dr. Arthur Clayton; Mr. A. T. King, B.Sc.; Mr. H. V. A. Briscoe, B.Sc.; Mr. E. G. Couzens, B.Sc.; Mr. F. P. Dunn, B.Sc.; Mr. H. F. V. Little, B.Sc.; and Mr. J. A. Pickard, B.Sc. Also to Mr. Arthur G. Francis, B.Sc., of the Government Laboratory; Mr. Lionel M. Jones, B.Sc., of the Birmingham Technical School; Miss Zelda Kahan, B.Sc., and Miss Gertrude Walsh, M.Sc.

Lastly, he is under great obligations to Dr. M. A. Whiteley, A.R.C.S., and Mr. F. P. Dunn, B.Sc., A.R.C.S., of the Imperial College, for the care and attention they have bestowed on the revision of the proof-sheets, and for the assistance they have rendered generally in the production of the work.

ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J. .	American Chemical Journal.
Amer. J. Pharm. .	American Journal of Pharmacy.
Amer. J. Sci. . .	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann Chim. anal. .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys. .	Annales de Chimie et de Physique.
Ann. Falsif. . . .	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm. . .	Archiv der Pharmazie.
Bentl. a. Trim. . .	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr. . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J. . .	The Bio-Chemical Journal.
Biochem. Zeitsch. .	Biochemische Zeitschrift.
Brewers J. . . .	Brewers Journal.
Bull. Imp. Inst. .	Bulletin of the Imperial Institute.
Bull. Soc. chim. .	Bulletin de la Société chimique de France.
Chem. Ind. . . .	Chemische Industrie.
Chem. News . . .	Chemical News.
Chem. Soc. Proc. .	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit. . . .	Chemiker Zeitung.
Chem. Zentr. . .	Chemisches Zentralblatt.
Compt. rend. . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J. . .	Dingler's polytechnisches Journal.
Färber-Zeit. . . .	Färber-Zeitung.
Flück. a. Hanb. .	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital. .	Gazzetta chimica italiana.
Jahrb. Min. . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing .	Journal of the Institute of Brewing.
J. Pharm. Chim. .	Journal de Pharmacie et de Chimie.
J. Phys. Chem. . .	Journal of Physical Chemistry.
J. pr. Chem. . . .	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers. . .	Journal of the Society of Dyers and Colourists.
Min. Mag. . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J. . . .	Pharmaceutical Journal.
Pharm. Zeit. . .	Pharmazeutische Zeitung.
Phil. Mag. . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . .	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc. . .	Proceedings of the Royal Society.
Rec. trav. chim. .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm. . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie

LIST OF CONTRIBUTORS

TO VOLUME I.

Dr. E. F. ARMSTRONG (*late of Messrs. Huntley and Palmers, Reading*). [AMYLANS, BREAD, CARBO-HYDRATES.]

Dr. G. H. BAILEY (*The British Aluminium Company, Kinlochleven, Argyll, N.B.*). [ALUMINIUM ALUMS, AND ALUMINIUM COMPOUNDS.]

G. S. BLAKE, Esq., A.R.S.M. [BARIUM; CALCIUM.]

BERTRAM BLOUNT, Esq., F.I.C., *Analytical and Consulting Chemist, London.* [CEMENT.]

HAROLD BROWN, Esq., *The Imperial Institute, London.* [BALATA.]

Dr. J. C. CAIN, *Editor of the Journal of the Chemical Society, London.* [ANILINE; ANILINE SALT; AZO-COLOURING MATTERS; BENZENE AND ITS HOMOLOGUES.]

W. H. COLEMAN, Esq., *Tar Works Chemist (late of Messrs. Hardman & Holden, Manchester).* [CARBOLIC ACID.]

Dr. HAROLD G. COLMAN, F.I.C., *Consulting and Analytical Chemist, London.* [AMMONIA.]

JAMES CONNAH, Esq., B.A., B.Sc., F.I.C., *The Government Laboratory, Custom House, London.* [ABSINTH; ABSINTHIN; ABSINTHOL; ARRACK; BRANDY; CHARTREUSE.]

C. F. CROSS, Esq., B.Sc., F.R.S. (*Messrs. Cross & Bevan, Consulting Chemists, London*). [CELLULOSE.]

Dr. W. DITTMAR, F.R.S., *late Professor of Chemistry in Anderson's College, Glasgow.* [BALANCE.]

THOMAS FAIRLEY, Esq., F.I.C., *Analytical and Consulting Chemist, Leeds.* [ASPIRATORS.]

JOHN GOLDING, Esq., F.I.C., *University College, Reading.* [CHEESE.]

Dr. A. D. HALL, M.A., F.R.S., *late of Rothamsted Experimental Station, Harpenden, Herts.* [CEREALS.]

Dr. W. D. HALLIBURTON, F.R.C.P., M.R.C.S., F.R.S., *Professor of Physiology, King's College, London.* [BILE; BLOOD; BONE.]

JOHN HERON, Esq., B.E. (R.U.I.), F.I.C., *late Consulting Chemist, London.* [BREWING.]

Dr. JOHN T. HEWITT, M.A., F.R.S., *Professor of Chemistry in the East London College.* [ACRIDINE DYE STUFFS.]

J. W. HINCHLEY, Esq., A.R.S.M., *Lecturer on Chemical Engineering, Imperial College of Science and Technology, South Kensington.* [AUTOCLAVE.]

JOHN HOLMES, Esq., *The Government Laboratory, London.* [ALCOHOLOMETRY.]

Dr. JULIUS HÜBNER, M.Sc., F.I.C., *Director of Dyeing and Paper-making Departments, Municipal School of Technology, Manchester.* [BLEACHING.]

H. W. HUTCHIN, Esq. (*The Cornish Consolidated Tin Mines, Camborne*). [ARSENIC.]

HERBERT INGLE, Esq., B.Sc., F.I.C., *late Chief Chemist to the Transvaal Agricultural Department.* [ALMOND; APPLE; APRICOT; ARGININE; ARROWROOT; ARTICHOKE; ASH; ASPARAGUS; AVOCADO PEAR; BANANA; BARLEY; BATATAS; BEAN; BEET-ROOT; BETAINE; BLACKBERRIES; BRAN; BREAD FRUIT; BUCK WHEAT; CABBAGE; CARROT; CASSAVA; CASTOR OIL SEEDS; CAULIFLOWER; CELERY; CHERRY; CHESTNUT.]

Dr. RUDOLF LESSING, *Consulting Chemist, London.* [BROMINE.]

VIVIAN B. LEWES, Esq., F.I.C., *late Professor of Chemistry in the Royal Naval College, Greenwich, S.E.* [ACETYLENE AS AN ILLUMINANT; BOILER INCRUSTATIONS AND DEPOSITS.]

Dr. JULIUS LEWKOWITSCH, M.A., F.I.C., *late Consulting and Analytical Chemist, London.* [ADIPOCERE; ANACARDIUM NUT; ARACHIS OIL; BASSIA OILS; BEN OIL; BONE FAT; BORNEO TALLOW; BRAZIL NUTS; CACAO BUTTER; CAMELINE OIL; CANDLES; CANDLE-NUT OIL; CASTOR OIL; CHAULMOOGRA OIL GROUP.]

C. A. MITCHELL, Esq. (*Messrs. Beaufoy & Co., South Lambeth Road, S.W.*). [AERATED OR MINERAL WATERS.]

Dr. GILBERT T. MORGAN, F.R.S., A.R.C.S., F.I.C., *City and Guilds of London Technical College, Finsbury, E.C.* [ACIDIMETRY AND ALKALIMETRY; ANALYSIS; CERIUM; CERIUM METALS AND EARTHS.]

L. MYDDELTON NASH, Esq., F.I.C. (*Messrs. Carson & Sons, Battersea*). [CASEIN.]

B. E. R. NEWLANDS, Esq., F.I.C. (*late of Messrs. Newlands Brothers, Analytical Chemists, London*). [ANIMAL CHARCOAL.]

A. G. PERKIN, Esq., F.R.S., F.I.C., *Clothworkers' Research Laboratory, University of Leeds.* [ALKANET; ANNATTO; ARCHIL; ASBARG; AURANORIN; BARBATIC ACID; BRAZIL WOOD; BUCKTHORN; BUTEA FRONDOSA; CATECHU; CATELLAGIC ACID; CHAY ROOT; CHESTNUT EXTRACT.]

Dr. F. MOLLWO PERKIN, *Consulting Chemist, London.* [ELECTROCHEMICAL ANALYSIS.]

Professor W. H. PERKIN, LL.D., F.R.S., and Dr. ROBERT ROBINSON, *Chemical Departments Universities of Oxford and Liverpool.* [ALIZARIN AND ALLIED COLOURING MATTERS.]

Dr. J. C. PHILIP, M.A., *Professor of Physical Chemistry, Imperial College of Science and Technology, South Kensington.* [CHEMICAL AFFINITY.]

J. A. PICKARD, Esq., B.Sc., A.R.C.S. [ACETINS; ALLYL.]

Dr. HENRY ROBINSON, M.A. [ANÆSTHETICS.]

Sir THOMAS K. ROSE, *The Royal Mint, London.* [ASSAYING.]

Dr. WALTER ROSENHAIN, F.R.S., *The National Physical Laboratory, Teddington.* [AMALGAM; ANNEALING.]

Dr. F. W. RUDLER, I.S.O., *late of the Museum of Economic Geology, Jermyn St., London.* [AGATE; CAIRNGORM.]

Dr. ROBERT SCHÜPPHAUS, *Consulting Chemist, New York.* [CELLULOID.]

Dr. ALFRED SENIER, F.I.C., *Professor of Chemistry, University College, Galway.* [ALOES; ARAROBA POWDER; BALSAMS; BLACK HELLEBORE ROOT; BROOM TOPS; CALUMBA; CAMPHORS; CASCARA SAGRADA; CASCARILLA BARK.]

L. J. SPENCER, Esq., M.A., *Mineralogical Department, British Museum, London.* [ABRASIVES; AGALITE; AGALMATOLITE; ALUM-SHALE; ALUNITE; ALUNOGEN; AMAZON-STONE; AMBER; AMBLYGONITE; AMETHYST; ANATASE; ANGLESITE; APATITE; ARAGONITE; ARGENTITE; ARGYRODITE; ASBESTOS; ATACAMITE; AZURITE; BARYTES; BAUXITE; BELLITE; BENITOITE; BERYL; BERZELIANITE; BERZELIITE; BISMITE; BISMUTHINITE; BISMUTITE; BLOODSTONE; BLUE IRON-EARTH; BOG IRON ORE; BOLE; BORNITE; BORONATROCALCITE; BOSTONITE; BOURNONITE; BRAUNITE; BROCHANTITE; BRÖGGERITE; BRUCITE; BUHRSTONE; CALCITE; CARBONITE; CARNOTITE; CASSITERITE; CELESTITE; CERARGYRITE; CERUSSITE; CHALCANTHITE; CHALK; CHALYBITE.]

GEORGE STUBBS, Esq., F.I.C., *The Government Laboratory, London.* [BUTTER.]

EDWARD R. TAYLOR, Esq., *Manufacturing Chemist, Penn Yan, N.Y., America.* [MANUFACTURE OF CARBON DISULPHIDE BY THE ELECTRIC FURNACE.]

MISS BEATRICE THOMAS, M.A., *Girton College, Cambridge.* [AMINES.]

Dr. M. A. WHITELEY, A.R.C.S., *Lecturer in Organic Chemistry, Imperial College of Science and Technology, South Kensington.* [ADENINE; ALANINE; ALLANTOIN; ALLOXAN; ALLOXANTIN; ARGINASE; ARGININE; ASPARAGINE; ASPARTIC ACID; CARNINE; CARNITINE; CARNOSINE.]

GEHEIMRAT PROFESSOR Dr. OTTO N. WITT, *late of the Polytechnic, Charlottenburg, Berlin.* [AZINES.]

Dr. W. P. WYNNE, F.R.S., F.I.C., A.R.C.S., *Firth Professor of Chemistry, University of Sheffield.* [AURIN AND ROSOLIC ACID.]

A

DICTIONARY

OF

APPLIED CHEMISTRY.

AAL, A'L, ACH, AI'CH. Native names for the roots of *Morinda tinctoria* and *M. citrifolia*, employed in various parts of India, under the general trade name of Suranji, as a dyestuff, more especially for dyeing reds, purples, and chocolates.

ABACA. A species of fibre derived from *Musa textilis* (Née), obtained mainly from the Philippine Islands, and used in the manufacture of mats, cordage, &c. It is also known under other names, including 'Manilla hemp,' 'Menado hemp,' 'Cebu hemp,' 'Siam hemp,' and 'White rope.' Less valuable fibres are obtained from other species of *Musa*, such as *M. sapientum* (Linn.), the banana and plantain, which yield banana fibre and plantain fibre.

ABIES. The generic name of the Silver Firs. *A. alba* (Mill.) [*A. pectinata* (DC.)] furnishes timber very similar to the white deal of *Picea excelsa*, the common spruce. It is the source of 'Strasburg turpentine,' containing free *abienic*, *abietric*, and *α-* and *β-abietinolic acids*, and an amorphous substance *abietoresen*, an ethereal oil of agreeable aromatic odour, a bitter principle and colouring matter (Tschirch und Weigel, Arch. Pharm. 1900, 238, 411).

A. Canadensis is the source of Canada balsam, which contains *canadic*, *canadolic*, and *α-* and *β-canadinolic acids*, an ethereal oil, *canadoresen*; and small quantities of succinic acid and a bitter substance. The acids contain no methoxyl groups and give the cholesterol reactions, including that of Tschugaeff (*l.c.* 1900, 238, 487).

ABIETENE. A hydrocarbon obtained by distilling the terebinthinate exudation of *Pinus sabiniana* (Doug.), a coniferous tree indigenous to California, and growing on the dry slopes of the foothills of the Sierra Nevada and on the hills along the coast, and known locally as the Nut pine or Digger pine. To procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil was met with in San Francisco as an article of commerce under the names of 'Abietene,' 'Erasine,' 'Aurantine,' and 'Thioline,' and was used for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colourless mobile liquid of powerful aromatic smell, recalling that of oil of oranges.

Abietene has been shown by Thorpe to consist almost entirely of *normal heptane*, C_7H_{16}, mixed with a small quantity of a resin to which its characteristic smell of orange oil is due (Thorpe, Chem. Soc. Trans. 35, 296; Schorlemmer and Thorpe, Phil. Trans. 174, 269; *v.* also Blasdale, J. Amer. Chem. Soc. 1901, 162).

Abietene is also the name given to the hydrocarbon which is obtained as an oil by the reduction of abietic acid (*q.v.*) (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1238; Kraemer and Spilker, Ber. 1899, 2953, 3614). Its formula is $C_{18}H_{28}$, and it is probably decahydroretene, as, when carefully purified, and reduced with phosphorus and hydriodic acid, it yields a fluorescent hydrocarbon identical with the dodecahydroretene of Liebermann and Spiegel (Ber. 1889, 780).

ABIETIC ACID. An acid obtained by digesting colophony with dilute alcohol and recrystallising the product from methyl alcohol (Maly, Annalen, 129, 54; 132, 249); or by saturating an alcoholic solution of colophony with hydrogen chloride and subsequently recrystallising the product (Flückiger, J. 1867, 727). It can also be obtained by distilling colophony under reduced pressure or with superheated steam (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1238). It occurs in resin spirit, from which it may be obtained by extraction with ether, shaking with sodium carbonate solution and then acidifying with acid. It is obtained in a purer condition by recrystallising from acetic acid; m.p. 166°–167° (Tschirch and Wollf, Arch. Pharm. 1907, 1); 153°–154° (Mach, Monatsh. 1893, 186). According to Easterfield and Bagley and Mach, it is a derivative of phenanthrene, and has the formula $C_{19}H_{28}O_2$, whilst Levy (Ber. 1906, 3043), Koritschoner (J. Soc. Chem. Ind. 1907, 641), Fahrion (J. Soc. Chem. Ind. 1907, 264), and Vesterberg (Ber. 1907, 120) represent its composition as $C_{20}H_{30}O_2$. According to Strecker

(Annalen, 150, 131), Duvernoy (Annalen, 148, 143), and Easterfield and Bagley (*l.c.*), abietic acid is identical with sylvic acid; it is not identical with pimaric acid, which yields abietic acid on distillation under reduced pressure. By distilling abietic acid under ordinary pressure, or, better, by treatment with hydriodic acid, carbon dioxide is evolved, the hydrocarbon *abietene* $C_{18}H_{28}$ being formed (E. and B. *l.c.*; Levy, *l.c.*; Kraemer and Spilker, Ber. 1899, 3614). Distillation with sulphur converts abietic acid into retene, $C_{18}H_{18}$ (E. and B., *l.c.*; Vesterberg, Ber. 1903, 4200). Oxidation with potassium permanganate yields an acid $C_{19}H_{16}O_3$, m.p. 123° (Mach, Monatsh. 1894, 627); and a method has been devised by Endemann (D. R. P. 183328; Chem. Zentr. 1907, i. 1607) to oxidise resinous materials, containing abietic acid, to resin acids and malonic acid.

Detection and Estimation.—The following co our reactions may be used for detecting abietic acid:—(1) 3 vols. of conc. hydrochloric acid and 1 vol. of ferric chloride sol. give a violet red colouration; (2) sulphuric acid dissolves abietic acid to a red solution; (3) when heated with dry chloroform, acetic anhydride and sulphuric acid, a purple red colour is produced changing through violet and blue to a greenish black (Mach. *l.c.*). In order to estimate abietic acid in resins, &c., 10 grms. of the substance are refluxed with 20–25 c.c. of 10 p.c. alcoholic potash for ½ hour on a water-bath; the resulting soap is decomposed with dilute hydrochloric acid, and the separated resin filtered off, washed with cold water and dried. It is then powdered and extracted with 50 c.c. of hot petroleum ether. From this solution abietic acid is precipitated by ammonia, filtered off, dried on the water-bath, and the ammonia expelled by gentle heating. The residue represents the amount of crude abietic acid in the sample (Rebs, Chem. Zentr. 1907, i. 997).

Abietic acid (or colophony) is used in assisting the growth of lactic or butyric ferments, as it favours the production of that which is present in the greater quantity and suppresses the other. It promises to be of great use in the fermentation industry in preventing infection (Effront, Compt. rend. 136, 1556), (*v.* COLOPHONY).

ABRASIVES. The various hard substances, chiefly of mineral origin, used for abrasive purposes fall naturally into the following groups, in which the hardness is roughly inversely proportional to the complexity of chemical composition.

Elements.—Diamond (*q.v.*) is the hardest of all substances (hardness = 10 on Mohs's scale). Inferior material of no use for gems is known as boart (or bort), and is crushed to powder and much used by lapidaries. Diamond powder is the only material with which diamond itself can be ground and polished. Embedded in the edge of a thin disc of soft iron, diamond powder is largely used for cutting gem-stones and thin sections of rock specimens, and also for slicing larger blocks of the harder ornamental stones. A black, compact variety of diamond known as carbonado ('carbonate' or 'carbon') is embedded in the steel crowns of rock-drills.

Amongst artificial products, steel and some other hard metals are used for abrasive purposes. The so-called crushed steel, made by quenching white-hot crucible steel, is used in the stone-cutting trade. Tantalum is an extremely hard metal and may in future find some application depending on hardness.

Carbides.—Carborundum[1] (*q.v.*) or silicon carbide, CSi (H. = 9½), is prepared artificially in the electric furnace from petroleum-coke and the purest quartz-sand, and is produced in large quantities (over 3000 tons in 1907) at Niagara Falls. It is largely made into sharpening stones and grinding wheels. In lapidaries' work it has to a certain extent taken the place of corundum; but although harder than corundum, it has the disadvantage of being more brittle, and it soon rubs to flour. Carbide of boron, CB_6, and silicide of boron, SiB_3, are also remarkable on account of their intense hardness (H. Moissan, Compt. rend. 118, 556).

Oxides.—Corundum (*q.v.*) Al_2O_3 is, next to diamond, the hardest of minerals (H. = 9). The impure variety, emery (*q.v.*), is not quite so hard. The crushed and graded material is made into corundum wheels and emery paper, and is much used in lapidaries' work. Artificial corundum, known by the trade-name of 'alundum,' is now manufactured in considerable amounts (about 3000 tons in 1907) at Niagara Falls, by fusing bauxite in an electric furnace. 'Corubin' is also an artificial corundum, formed as a by-product in the Goldschmidt thermite process.

Quartz (*q.v.*) SiO_2 (H. = 7), and its several varieties find extensive applications. Millstones and grindstones are made of quartz-rock, quartzite, burrstone (or buhrstone), grit, or sandstone (*q.v.*); while scythe-stones, oilstones (*q.v.*), and whetstones (*q.v.*) consist of hornstone, lydian-stone and other compact varieties of quartz. In the form of sand, quartz is used as a sand-blast, in scouring-soap, for cutting and grinding marble, making sand-paper, &c. Tripoli or infusorial earth is a powdery variety of opal (hydrated silica), and is used for polishing.

Silicates.—Garnet (*q.v.*) (H. = 6½–7½) is used for making 'emery' paper and cloth; and felspar (*q.v.*) (H. = 6) is also used to a small degree. Silicate rocks are employed to a small extent; *e.g.* pumice for polishing, and the millstone lava (leucite-nepheline-tephrite) of Niedermendig on the Rhine, for millstones. L. J. S.

ABRASTOL or *Asaprol - Etrasol.* Trade names for the calcium salt of β-naphthol-sulphonic acid, $Ca(C_{10}H_7OSO_3)_2,3H_2O$, used in the clarification and preservation of wines. The maximum quantity needed for this purpose is 10 grms. per hectolitre. According to Noelting and Dujardin-Beaumetz and Stackler, the substance is harmless from a hygienic point of view (see Mon. Sci. 1894, 8, 257; J. Soc. Chem. Ind. 1894, 177, 534). To detect its presence, Sanglé-Ferrière proceeds as follows (Compt. rend. 1893, 117, 796): 200 c.c. of the wine is boiled for an hour in a reflux apparatus with 8 c.c. of hydrochloric acid, when the abrastol is hydrolysed to β-naphthol, which may be extracted with benzene, and the residue left after distilling the benzene sol. taken up with chloroform. A fragment of potash is dropped

[1] So named by E. G. Acheson, in 1893, from carbon and corundum, because before it had been analysed, it was thought to be a compound of carbon and alumina.

into the chloroform solution, which is boiled for 2 mins., when a blue colouration is produced changing to green and finally becoming yellow. 0·1 grm. per litre may thus be detected. The presence of abrastol in no way vitiates the determination of potassium sulphate (J. Soc. Chem. Ind. 1894, 177). Sinibaldi (Mon. Sci. 7, 842) has given the following method: 25 c.c. of the wine are neutralised by ammonia and shaken with 25 c.c. of amyl alcohol. After separation, the amyl alcohol is boiled to expel ammonia, and when cold is shaken with 0·25 c.c. ferric chloride sol. A grey-blue colouration denotes abrastol. Gabutti (Chem. Zentr. 1904, 2, 370) proceeds in a similar way, but instead of ferric chloride, employs phosphoric acid and formaldehyde solution, when, in presence of abrastol, a green fluorescence is produced. (For other methods, *v.* Sanna Pintus, J. Soc. Chem. Ind. 1900, 933; Briand, Compt. rend. 1894, 118, 925; Carletti, Chem. Zentr. 1909, 2, 72. For colour reactions, *v.* Barral, J. Pharm. Chim. 1903, 18, [5] 206; Salomone, Chem. Zentr. 1907, i. 306.)

(For a review of the various methods of detection, *v.* Vitali, Apoth. Zeit. 1908, 23, 507; J. Soc. Chem. Ind. 1908, 830.)

ABRAUM SALTS. (Ger. *Abraumsalze*: 'salts to be removed.') The mixed salts found overlaying the rock-salt deposit at Stassfurt, in Prussia. These consist mainly of rock-salt; *Carnallite*, a double chloride of potassium and magnesium; *Sylvine*, or potassium chloride; and *Kieserite*, or magnesium sulphate, *v.* POTASSIUM.

ABRIN. A brownish yellow soluble substance obtained from the seeds of *Abrus precatorius* (*Indian liquorice* or *Jequirity*). Contains a poisonous proteid, resembling, if not identical with, ricin. Lethal dose, according to Kobert, is only 0·00001 grm. per kilo body-weight: *i.e.* 1 to 100,000,000.

ABSINTH. (*Absinthe*, Fr.; *Wermuthextract*, Ger.) One of the best-known liqueurs or cordials (*q.v.*), is made chiefly at Lyons, Montpellier and Pontarlier in France, and until quite recently (*vide infra*) at Neufchâtel in Switzerland. It is a highly intoxicating spirituous liquor flavoured with oil of wormwood (*Artemisia absinthium*, nat. ord. *Compositæ*) and other essential oils as angelica, anise, cinnamon, cloves, fennel, hyssop, peppermint, &c. (*v.* OILS, ESSENTIAL).

There are three distinct processes in the manufacture of absinth, viz.: maceration, distillation, and colouration. The leaves and flowertops of *Artemisia absinthium*, together with the other flavouring ingredients (which vary in kind and quality according to the requirements of the different manufacturers) are digested with spirit for periods varying from 12 hours to 10 days, according to the temperature of the infusion and the strength of the spirit used. The French manufacturers, as a rule, digest for short periods at the temperature of an ordinary water bath, and with spirit containing about 85° alcohol, whilst the Swiss maceration process was conducted at air temperature with spirit somewhat below British 'proof' strength, or about 50° alcohol.

The infusion is distilled and the distillate transferred to the colouring vessel containing small absinth leaves, balm and hyssop, dried and finely divided. This vessel is hermetically sealed and is gently heated by steam to a temperature of 60° in order to extract chlorophyll. After cooling, the green liquor is drawn off, and strained, if necessary, through a hair sieve. The colouring is sometimes separately prepared and added as required to the colourless distillate. Occasionally the latter is sweetened by the addition of about 5 p.c. by weight of crushed white sugar. Chlorophyll for imparting the green colour to absinth (and other liqueurs) is frequently obtained from nettles, parsley, and spinach, and is free from objection provided the vegetable matter is sound.

On keeping, genuine absinth assumes the yellowish tint appreciated by connoisseurs, and its qualities generally are improved by age. Many objectionable varieties of absinth are, however, on the market, made from inferior spirit, to which essences and resins are added, the former to give a fictitious flavour and the latter to produce the opalescence which occurs in genuine absinth on the addition of water, owing to the liberation of the essential oils, resinous bodies, and colouring matters derived from the plants and seeds used in its manufacture. Other colouring matters than chlorophyll are also employed, as indigo, sulphate of copper, picric acid and turmeric or other vegetable colour. Gum benzoin, guiacum and rosin are also used to produce 'milkiness' on dilution, and even chloride of antimony is said to have been employed for this purpose.

To detect adulteration it is usually sufficient to determine the essential oils, resins, and colouring matters (*vide* Hubert, Ann. Chim. anal. 6, 409, and Nivière and Hubert, Mon. Sci. 1895, 566). According to Hubert, absinth has a specific gravity of 0·8966 to 0·9982, and alcoholic strength of 47 to 72 p.c. by volume of absolute alcohol. The average results of twelve samples expressed as grams per litre were as follows: essential oils, 1·5 to 5·0; extractive, 0·36 to 1·72; acids, 0·024 to 0·288; aldehydes, 0·005 to 0·155; furfurol, 0·0002 to 0·007; ethers, 0·005 to 0·123. The strength of absinth as imported into the United Kingdom varies from 'proof' to about 20 over proof, and rather more than 3000 gallons are imported annually.

Although genuine absinth, taken in moderation, has valuable qualities as a cordial, stomachic, and febrifuge, its characteristic bitter principle, absinthiin (*q.v.*), is an active poison, having a very injurious effect upon the nervous system of those addicted to the habitual and immoderate consumption of absinth. Legal measures have therefore been taken in various European countries to control, restrict, or even prohibit its sale. In France, liqueurs may not contain more than 1 gram per litre of oil of wormwood or other oil of similar toxic nature, whilst in Belgium the manufacture and sale of absinth have been entirely prohibited. A similar prohibition was enforced in 1910 by the Swiss Government. J. C.

ABSINTHIN or **ABSINTHIIN** $C_{15}H_{20}O_4$. The bitter principle extracted from the dried leaves of large absinth or wormwood (*Artemisia absinthium*) is an active poison. and it is to its presence in oil of wormwood that the toxic effect of absinth (*q.v.*) appears to be due.

Various formulæ have been assigned to this

substance, the differences being due to the difficulty of obtaining it in a pure state (Mein, Annalen, 8, 61; Luck, Annalen, 78, 87; Kromayer, Arch. Pharm. [2] 108, 129).

Pure crystallised absinthiin was first isolated by Duquesnel (Bul. de Therapeutique, 107, 438). Senger obtained absinthiin as a pale yellow amorphous substance melting at 65° and having the empirical formula $C_{15}H_{20}O_4$. This formula was confirmed later by Bourcet, who found that the pure substance crystallises in fine white prismatic needles melting at 68°, the amorphous form and lower melting-point found by Senger being probably due to traces of a resinous impurity.

According to Senger and Bourcet, absinthiin is a glucoside, free from nitrogen, and is decomposed by the action of dilute acids, or even by boiling with water, into dextrose, a volatile oil, and a solid resinous body of the aromatic series. It is soluble in alcohol, ether, chloroform, or benzene; difficultly soluble in light petroleum, water, though more soluble in cold than in boiling water. It gives a precipitate with tannic acid and with gold chloride, which is reduced on warming; yields volatile fatty acids on oxidation with nitric acid, and oxalic and picric acids with potassium chromate and sulphuric acid. With Fröhde's reagent it gives a brown colour, changing to violet, then blue; and with sulphuric acid brown, passing through green to blue (Senger, Arch. Pharm. 230, 103; and Bourcet, Bull. Soc. chim. [3] 19, 537). J. C.

ABSINTHOL $C_{10}H_{16}O$. The essential principle of oil of wormwood derived from *Artemisia absinthium* (nat. ord. *Compositæ*), a plant indigenous to most European countries and comparatively recently introduced into the United States of America, whence increasing supplies of the cheaper qualities of wormwood oil are now obtained.

Although the oil obtained by the distillation of wormwood has been known for at least four centuries, its chemical composition was first systematically investigated in 1845, when Leblanc (Compt. rend. 21, 739) showed that its principal constituent, boiling at 203°, has the formula $C_{10}H_{16}O$. This was confirmed later by Gladstone and other investigators (Chem. Soc. Trans. 17, 1), and by Beilstein and Kupffer (Annalen, 170, 290), who gave to the product the name '*absinthol*,' and identified its dehydration product with *cymene*.

Semmler (Ber. 25, 3350) proved absinthol to be a ketone identical with thujone or tanacetone, which occurs largely in other essential oils, as oil of tansy, sage, and *Artemisia barelieri*. It is a colourless oily liquid of pleasant odour, strongly dextrorotatory (about +68°), boils at 203°, density 0·9126 at 20°, and refractive index 1·4495.

Though isomeric with camphor, it differs from that body in combining with sodium bisulphite and in not being converted into camphoric acid by means of nitric acid, nor into camphocarboxylic acid by treatment with carbon dioxide and sodium. With melted potash it gives a resin, but no acid. When heated with P_2S_5 and $ZnCl_2$ it yields cymene (Beilstein and Kupffer, Ber. 6, 1183; Annalen, 170, 290; Wright, Chem. Soc. Trans. 27, 1 and 319; Semmler, Ber. 25, 3343 and 27 895). J. C.

ABUTILON INDICUM (Sweet), **PETAREE** or **TUBOCUTY.** The bark of this malvaceous tree consists of long, thin, tough fibrous strips (bast fibres), and, according to Dymock (Pharm. J. [3] 8, 383) and others, is worthy of attention as a source of fibre.

ABYSSINIAN GOLD. A yellow alloy of 90·7 parts of copper and 8·3 of zinc. The ingot is plated on one side with gold, and is then rolled out into sheets, from which articles of jewellery are formed in the usual way, the amount of gold on the finished article varying from 0·03 to 1·03 p.c. Known also as *Tulmi gold*. The term is sometimes applied in trade to Aluminium Bronze.

ACACIA CATECHU (Willd) or **KHAIR** is a tree growing in various parts of India. Its unripe pods and wood, by decoction, yield a catechu (Agricult. Ledger, 1895, No. 1, and 1896, No. 35) known by the name of Cutch or Kutch, which must not be confounded with the officinal catechu (*Catechu pallidum*). It is used in the preparation of some leathers and by dyers. The timber is also used for constructional and other purposes.

ACACIA GUM *v.* GUMS.

ACANTHITE. A form of silver sulphide found at the Enterprise mine, near Rico, in black crystals of orthorhombic habit (Chester, Zeitsch. Kryst. Min. 1896, 26, 526).

ACAROID RESIN or **BOTANY BAY RESIN** *v. Xanthorrhœa Balsams*, art. BALSAMS.

ACCIPENSERINE. A protamine belonging to the sturine group found in the testis of *Accipenser stellatus*. Composition of the sulphate: $C_{35}H_{72}O_9N_{18},4H_2SO_4$ (Kuraéèff, Zeitsch. physiol. Chem. 1901, 32, 197).

ACENAPHTHENE $C_{12}H_{10}$, *i.e.* $C_{10}H_6:C_2H_4$. A crystalline substance found in coal-tar oil (Berthelot, Bull. Soc. Chim. [2] 8, 226). Obtained by cooling the fraction of heavy coal-tar oil boiling between 260° and 270°. On recrystallising the solid product from alcohol, acenaphthene is obtained in long needles, m.p. 95° (Behr and Dorp, Annalen, 172, 265), 103° (Schiff, Annalen, 223, 263); b.p. 278°; 229·5° (Perkin, Chem. Soc. Trans. 69, 1196).

For its Absorption Spectrum, *v.* Baly and Tuck (Chem. Soc. Trans. 1908, 1902); Heats of Solution (Speyers, Amer. Chem. J. 18, 146); Magnetic Rotation (Perkin, Chem. Soc. Trans. 1896, 1088); Refraction and Dispersion (Pellini, Gazz. chim. ital. 31, i. 1); Similarity in form to acenaphthylene (Billows, Chem. Zentr. 1903, ii. 44).

Is reduced by hydrogen in presence of nickel to tetrahydroacenaphthene (Sabatier and Senderens, Compt. rend. 132, 210, and 566); with NiO_2 to tetrahydro- and dekahydroacenaphthene (Ipatjew, Ber. 41, 997).

With potassium dichromate and acetic acid yields naphthalic acid and acenaphthenequinone (Graebe and Gfeller, Ber. 25, 652; Jaubert, Gazz. chim. ital. 25, i. 245).

Derivatives.—Oxygenated (Graebe and Gfeller, Annalen, 276, 1; Hodgkinson, Chem. Soc. Proc. 1896, 110); with sulphur (Dziewonski, Ber. 36, 962; Rehlander, Ber. 36, 1583); styphnate (Gibson, Chem. Soc. Trans. 1908, 2098).

ACETAL $C_6H_{14}O_2$, or $CH_3{\cdot}CH(OC_2H_5)_2$ (Döbereiner, Gm. 4, 805 · Liebig, Annalen, 5, 25; 14, 156; Stas, Ann. Chim. Phys. [3] 19, 146;

Wurtz, Ann. Chim. Phys. [3] 48, 70; Geuther, Annalen, 126, 63).

To prepare acetal by Wurtz's method, 2 parts alcohol are added to a mixture of 3 parts manganese dioxide, 3 parts sulphuric acid and 2 parts water, and, after the effervescence first produced has subsided, the whole is heated at 100° until 3 parts have distilled over. The product is then fractionally distilled, and two portions, one boiling below 80° and the second boiling at 80°–95°, are collected.[1] Each fraction is treated with solution of calcium chloride and the ethereal layer which separates is distilled. The product contains aldehyde and ethyl acetate in addition to acetal; to remove these it is shaken with concentrated aqueous potash, the brown liquid separated from the aqueous layer is distilled, and the distillate shaken with calcium chloride. It is then heated with twice its volume of concentrated aqueous soda in sealed tubes at 100° for 24 hours, separated from the soda, distilled, the distillate again rectified: the fraction 100°–105°, which constitutes the greater portion, is acetal.

In addition to its formation as a by-product in the oxidation of alcohol, acetal can also be obtained from a mixture of acetaldehyde (1 vol.) and absolute alcohol (2 vols.) (1) by heating with acetic acid (½ vol.) for 12 hours at 100° (Geuther, Annalen, 126, 63); (2) by cooling in a freezing mixture, passing dry hydrogen chloride to saturation, and decomposing the resulting monochlorether with sodium ethoxide (Wurtz and Frapolli, Compt. rend. 67, 418; Annalen, 108, 223); or (3) by cooling a mixture of equal volumes to −21°, and passing a current of pure hydrogen phosphide for 24 hours (Engel and Girard, Compt. rend. 92, 692; J. 1880, 694).

Acetal is a colourless liquid with agreeable odour: b.p. 104°, and sp. gr. 0·821 at 22·4° (Stas, Annalen, 64, 322); b.p. 103·7°–104·3° at 744·4 mm., and sp. gr. 0·8314 at 20°/4° (Brühl, Annalen, 203, 25). It is soluble in 18 vols. of water at 25°, and the solubility increases as the temperature rises. Acetal is miscible in all proportions with alcohol and ether, does not reduce ammoniacal silver solution, and is unaltered on exposure to air; platinum black, however, oxidises it first to acetaldehyde and subsequently to acetic acid.

Acetal does not give the iodoform reaction until shaken with a few drops of hydrochloric acid, whereby the acetal is hydrolysed to alcohol and aldehyde.

Derivatives.—Mono-, di-, and trichloracetal are obtained as intermediate products in the preparation of chloral by passing chlorine through 80 p.c. alcohol (Lieben, Ann. Chim. Phys. [3] 52, 313; Paternò, Compt. rend. 67, 765). According to Krey (J. 1876, 475), a better yield of these derivatives is obtained if a mixture of 2 parts absolute alcohol, 3 parts manganese dioxide, 3 parts sulphuric acid, and 2 parts water is heated until ⅔ of the liquid has distilled over and chlorine is passed through the well-cooled distillate until it shows signs of turbidity. In either case the product is washed with water, dried over calcium chloride, and submitted to fractional distillation. The fraction 80°–120° contains chiefly aldehyde and compound ethers, 120°–170° chiefly monochloracetal, 170°–185° dichloracetal (Lieben, *l.c.*), and the fraction boiling above 185° contains trichloracetal (Paternò, *l.c.*). These compounds may then be obtained in the pure state by repeated fractionation.

A better method of obtaining monochloracetal is by passing chlorine through well-cooled 94–99 p.c. alcohol until the chlorinated product has a sp.gr. 1·02–1·03 at 25°. Half the original volume of alcohol is added and the mixture heated a few hours at 50°–60°. The free acid is removed by calcium carbonate; the oil washed with water, dried and fractionated. The proportion of di- and tri-chloro-derivatives formed depends on the amount of chlorine added (Fritsch, Annalen, 279, 288).

Monochloracetal $CH_2Cl.CH(OC_2H_5)_2$ (Lieben, Annalen, 146, 193; Paternò, Mazzara, Ber. 6, 1202; Klien, J. 1876, 336; Natterer, Monatsh. 3, 444; 5, 497; Wislicenus, Annalen, 192, 106; Frank, Annalen, 206, 341) is a colourless liquid, naving an aromatic ethereal odour; b.p. 155°; sp.gr. 1·0418 at 0°, 1·026 at 15° (Klien): 156°–158° (Autenrieth, Ber. 24, 159). When heated with bleaching powder it yields di- and trichloracetal, chloroform, and chlorinated acetaldehyde (Goldberg, J. pr. Chem. [2] 24, 107).

Dichloracetal $CHCl_2.CH(OC_2H_5)_2$ (Jacobsen, Ber. 4, 217; Pinner, Ber. 5, 148; Annalen, 179, 34; Krey, *l.c.*; Paternò, Annalen, 149, 372; 150, 134); b.p. 183°–184°; sp.gr. 1·1383 at 14°. When treated with hydrocarbons it forms compounds of the type $CHX_2.CCl_3$ (Fritsch, Annalen, 279, 219; Wiechell, Annalen, 279, 337; Buttenberg, Annalen, 279, 324).

Trichloracetal $CCl_3.CH(OC_2H_5)_2$ (Byasson, Bull. Soc. chim. 32, 304; Wurtz, Frapolli, J. 1872, 438); b.p. 197°; 204·8° at 758·7 mm. Paternò, Pisati J. 1872, 303); sp. gr. 1·2813. When heated with concentrated sulphuric acid it yields chloral.

Trichloracetal $C_6H_{11}Cl_3O_2$. Obtained by the action of chlorine on alcohol (Lieben, Paternò, Krey, *l.c.*); crystallises in monoclinic needles resembling caffeine; m.p. 89°.

Monobromacetal (Pinner, Ber. 5, 149; Wislicenus, Annalen, 192, 112; Fischer a. Lundsteiner, Ber. 25, 2551; Freundler a. Ledru, Compt. rend. 1905, 140, 794); b.p. 81°–82° at 27–28 mm. (Freundler). According to F. a. L. a cheap method of making monobromacetal is by brominating paraldehyde at 0° with constant shaking; mixing with absolute alcohol, and after standing 12 hours pouring into an ice-cold sol. of potassium carbonate. The separated oil is dried and fractionated *in vacuo*.

Monoiodoacetal, b.p. 100° at 10 mm.; sp. gr. 1·4944 at 15° (Hesse, Ber. 1897, 30, 1438).

ACETALS (Wurtz, Ann. Chim. Phys. [3] 48, 370). The acetals are a group of compounds formed by the combination of 1 mol. of an aldehyde with 2 mols. of an alcohol, and the elimination of the elements of 1 mol. of water. They are generally obtained as by-products in the preparation of aldehydes by the oxidation of the corresponding alcohols, the aldehyde at the moment of formation uniting with the alcohol, and this tendency to combine is much increased if acetic acid is present (Geuther, Annalen, 126, 65), or if pure hydrogen phosphide is passed through the cooled mixture of aldehyde and

[1] The b.p. is given as in the original paper, but, inasmuch as b.p. of acetal is 104°, it seems probable that 95° is a misprint for some higher temperature—say 105°.

alcohol (Girard, Compt. rend. 91, 629; J. 1880, 695).

They are formed readily by the interaction of aldehydes with very dilute alcoholic hydrochloric acid (Fischer and Giebe, Ber. 30, 3053; 31, 545). Ketonic and aldehydic acetals, both aliphatic and aromatic, are formed by the interaction of nascent orthoformic ester and the necessary ketone or aldehyde in the presence of hydrochloric acid (Claisen, Ber. 31, 1010; Annalen, 237, 269).

The acetals are liquids having aromatic odours, and are sparingly soluble in water, from which they can again be separated on addition of concentrated calcium chloride solution. They are readily soluble in alcohol and ether; their vapours or their solutions in alcohol benzene or acetones slowly harden dry gelatin films (Beckmann and Scharfenberger, Chem. Zentr. 1896, ii. 930). When heated in a closed tube with glacial acetic acid, the corresponding aldehyde is obtained (Beilstein, Annalen, 112, 239). According to Bachmann (Annalen, 218, 45) the series of acetals can be descended by heating any member of the group with an alcohol containing a smaller number of carbon atoms than is present in its alcohol residue; for example, diethylacetal and methyl alcohol yield dimethylacetal and ethyl alcohol; but the reverse change, if it occurs at all, results in the production of very small quantities of the higher acetal. Delépine (Compt. rend. 1901, 132, 331, 968) finds, however, that when some acetals are boiled with any alcohol in the presence of a few drops of hydrochloric acid, a balanced reaction takes place. Thus whether methylal is heated with amyl alcohol or diamyl formal with methyl alcohol, the result is the same, the products consisting of a mixture of methylal, diamyl formal, methyl and amyl alcohols and the mixed acetal $MeO{\cdot}CH_2{\cdot}OC_5H_{11}$, the products of higher molecular weight predominating. Mixed acetals—that is, acetals containing two different alcohol residues—described by Bachmann (*l.c.*), consist of mixtures of molecular proportions of two distinct acetals (Rübencamp, Annalen, 225, 271; Fritsch and Schumacher, Annalen, 279, 308), but Delépine (*l.c.*) seems to have obtained such acetals and also their chloro- derivatives. The latter have also been obtained by Magnamini (Gazz. chim. ital. 16, 330).

The following acetals have been prepared: methylal, which is an excellent solvent for many organic compounds (Kane, Annalen, 19, 175; Brühl, Annalen, 203, 12); ethylidene-dimethyl (Arlsberg J. 1864, 485), -dipropyl, and -di*iso*butyl (Girard, J. 1880, 695), and -di*iso*amyl ether (Arlsberg, J. 1864, 486); propylidenedipropyl ether (Schudel, Monatsh. 5, 247); *iso*butylidenediethyl ether (Oeconomides, Bull. Soc. chim. 35, 500); and amylidene-dimethyl, -diethyl, and -di*iso*amyl ether (Arlsberg, *l.c.*). Glycolacetal, a derivative of glycolaldehyde, has also been prepared (Pinner, Ber. 5, 150; Varley, Chem. Zentr. 1899, ii. 919).

A large number of halogen alkyl and other acetal compounds have been prepared (Fischer, Ber. 26, 464; 41, 2860; 42, 1070; Fritsch (*l.c.*); Wolff, Ber. 21, 1481; Wohl, Ber. 21, 616; 22, 568, 1353; Wohl and Lange, Ber. 40, 4727; Heller, Löb, Alexander, Ber. 27, 3097, 3093, 3102; Fosse and Etlinger, Compt, rend. 130, 1194; Delépine, *l.c.* and Compt. rend. 131, 745; Stollé, Ber. 35, 1590; Oddo and Mameli, Gazz. chim. ital. 33, ii. 373; Atto, R. Acad. Linci, 1905, [v] 14, ii. 587; Freundler, Compt. rend. 138, 289; Bull. Soc. chim. 1907, [iv] 1, 66; Tschitschibabin, J. pr. Chem. 1906, [ii.] 73, 326; Paal and Gember, Arch. Pharm. 246, 306; Arbusoff, J. Russ. Phys. Chem. Soc. 40, 637; Smiles, Chem. Soc. Trans. 1909, 1000). The mono- and di-acetal derivatives of catechol (pyrocatechin) are obtained by heating the monosodium derivative of catechol with monochloracetal (Moreu, Compt. rend. 126, 1656).

ACETALDEHYDE *v.* ALDEHYDES.

ACETAMIDE C_2H_5NO, or $CH_3{\cdot}CONH_2$.

(Hofmann, Ber. 15, 980; Schulze, J. pr. Chem. [2] 27, 512; Keller, J. pr. Chem. [2] 31, 364; Aschan, Ber. 31, 2344; Kündig, Annalen, 105, 277; Abel, J. Soc. Chem. Ind. 1899, 515.) Acetamide is usually prepared by the dry distillation of ammonium acetate; a better yield (91·7 p.c.) and a purer product is obtained by distilling ammonium diacetate in the special apparatus described by François (J. Pharm. Chim. 23, 230). Between 135° and 195° acetic acid and water are evolved, and at 195°–222° some acetamide passes over. When the temperature remains constant at 222° the distillation is stopped, the residue being pure acetamide. A nearly theoretical yield is obtained by saturating a mixture of ethyl acetate and ammonia with dry ammonia gas at −10°, and after standing, fractionating *in vacuó* (Phelps, Amer. J. Sci. 24, 429).

Acetamide forms white hexagonal crystals which are odourless when pure, and melt at 81°–82° (Hofmann, Ber. 14, 2729; Mason, Chem. Soc. Trans. 1889, 107; Meyer, Ber. 22, 24; Forster, Chem. Soc. Trans. 1898, 791; Nicol, Zeitsch. anorg. Chem. 15, 397), boils at 222° (cor.) [Kündig], is readily soluble in water, and when heated with acids or alkalis is converted into acetic acid and ammonia (Coninck, Compt. rend. 121, 893; 126, 907; 127, 1028; Dunstan a. Dymond, Chem. Soc. Trans. 1894, 220; Guebet, Compt. rend. 129, 61). Chlorine, led into fused acetamide, yields acetchloramide $CH_3{\cdot}CONHCl$; and bromine, in the presence of dilute aqueous potash or soda yields acetbromamide, which on distillation with concentrated aqueous soda is converted into methylamine (Hofmann, Ber. 15, 408); Buchner and Papendieck, Ber. 25, 1160; Selivanoff, Ber. 26, 423; François, Compt. rend. 147, 680; 148, 173; Behrend a. Schreiber, Annalen, 318, 371). Acetamide acts both as a base and an acid (Pinner and Klien, Ber. 10, 1896), combining with hydrogen chloride or nitric acid, and forming compounds in which a metal takes the place of one atom of hydrogen, as $C_2H_3O{\cdot}NHAg$ (Strecker, Annalen, 103, 321; Tafel and Enock, Ber. 23, 1550; Blacher, Ber. 28, 432; Hofmann and Bagge, Ber. 41, 312; Titherley, Chem. Soc. Trans. 1897, 467). According to Forster (Chem. Soc. Trans. 1898, 783), mercury acetamide is a powerful dehydrogenising agent and owing to its tendency to exchange its mercury for hydrogen when the latter is attached to nitrogen, particularly when hydroxyl groups are in proximity, it can be employed as a convenient means of detecting primary and secondary hydrazines and primary hydroxylamines. It has also a

marked tendency to form additive compounds (Morgan, Chem. Soc. Proc. 1906, 23). The hydrogen in the NH_2 group has also been replaced by alkyl groups (Titherley, Chem. Soc. Trans. 1901, 396, 411, 413). Acetamide forms molecular compounds of the type $CH_3{\cdot}CONH_2{,}X$, where X = an organic or inorganic acid or an inorganic salt (Titherley, *l.c.*; Topin, Ann. Chim. Phys. [7] 5, 99). When acetamide is treated with formaldehyde, paraldehyde, or trioxymethylene, condensation products of the type $R{\cdot}NH{\cdot}CH_2OH$ are obtained; these products are of value as antiseptics and as solvents for uric acid (J. Soc. Chem. Ind. 1906, 283). Mono-, di-, and trichloracetamide (Willm, Annalen, 102, 110; Geuther, J. 1864, 317; Pinner and Fuchs, Ber. 10, 1066; Malaguti, Annalen, 56, 286; Cloëz, Annalen, 60, 261; Bauer, Annalen, 229, 165; Dootson, Chem. Soc. Trans. 1899, 171; Swartz, Chem. Zentr. 1899, [i.] 588; Clermont, Compt. rend. 133, 737). Bromo-dialkyl-acetamide (J. Soc. Chem. Ind. 1904, 1238) and other halogen derivatives have also been prepared (Selivanoff, J. Russ. Phys. Chem. Soc. 24, 132; Broche, J. pr. Chem. [2], 50, 97; Conrad, Ber. 29, 1042; Zinke and Kegel, Ber. 23, 230; Willstätter, Ber. 37, 1775; Steinkopf, Ber. 41, 3571; Swartz, *l.c.*; Francesconi, Gazz. chim. ital. 33, 226; Ratz, Monatsh. 1904, 25, 687; Einhorn, Annalen, 343, 203; Finger, J. pr. Chem. 1906, [ii.] 74, 153).

The acetamido β-naphthaquinones and some of their halogen derivatives which may be used in dyeing (Kehrmann and Zimmerli, Matis, and Locker, Ber. 31, 2405; Kehrmann and Aebi, Ber. 32, 932; Kehrmann and Wolff, Ber. 33, 1538) and other acetamide derivatives have been prepared (J. Soc. Chem. Ind. 1894, 60; Lumière, Bull. Soc. chim. 1903, iii. 30, 966; Ratz, Monatsh. 26, 1487; Miolati, Gazz. chim. ital. 23, 190).

Diacetamide $C_4H_7NO_2$, or $NH(C_2H_3O)_2$ and its derivatives (*see* Gautier, Z. 1869, 127; Hofmann, Ber. 14, 2731; Hentschel, Ber. 23, 2394; Curtius, Ber. 23, 3037; Mathews, Amer. Chem. J. 20, 648; König, J. pr. Chem. 1904, [ii.] 69, 1; Troeger, J. pr. Chem. 69, 347; *Triacetamide* $C_6H_9NO_3$, or $N(C_2H_3O)_3$ and its derivatives (*see* Wichelhaus, Ber. 3, 847).

ACETANILIDE $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$, also known as *Antifebrin*, is prepared by heating together glacial acetic acid and aniline for some time.

By substituting thioacetic acid for acetic acid the reaction proceeds more rapidly and at a lower temperature (Pawlewski, Ber. 1898, 661). Acetanilide may also be prepared by heating 1 part of aniline with 1¼ parts of dilute acetic acid or of crude pyroligneous acid under pressure at 150°–160° (Matheson & Co., Eng. Pat. 6220 and D. R. P. 98070; J. Soc. Chem. Ind. 1897, 559).

The substance melts at 114·2° (Reissert, Ber. 1890, 2243), at 115°–116° (Hantzsch and Fresse, Ber. 1894, 2529), and boils without decomposition at 303·8° (corr.) (Pictet and Crépieux, Ber. 1888, 1111), at 305° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1216); it is soluble in hot water, alcohol, or ether.

Acetanilide is hydrolysed at 100° by caustic potash or by hydrochloric acid, but not by sulphuric acid (Hantzsch and Fresse, Ber. 1894, 2529); it is rapidly decomposed by chromic acid, liberating carbon dioxide, and producing colouring matters (De Coninck, Compt. rend. 1899, 503). It reacts with zinc chloride at 180° with the formation of the yellow dye *flavaniline* (Braütigam, Pharm. Zeit. 44, 75).

Acetanilide is present in the urine of cows (Petermann, Ann. Chim. anal. 1901, 165). It is largely used in headache powders. For methods of estimation *v.* Puckner, Ph. Rev. 1905, 302, and Seidell, Amer. Chem. J. 1907, 1091. The following reactions may be used for detecting its presence: (1) bromine water added to a solution of acetanilide in acetic acid gives a white crystalline precipitate of *p*-bromacetanilide, m.p. 167°; (2) evaporation of a solution to dryness with mercurous nitrate gives a green mass, changing to blood red on addition of a drop of concentrated sulphuric acid; (3) ferric chloride gives no blood-red colouration with acetanilide, thus distinguishing it from phenacetin and antipyrine.

Derivatives.—Chloracetanilides (Jones and Orton, Chem. Soc. Trans. 1909, 1056); Nitroacetanilides (Holleman and Sluiter, Rec. trav. chim. 1906, 208).

ACETIC ACID. *Acide Acétique. Essigsäure Acidum Aceticum.* $C_2H_4O_2$ *i.e.* $CH_3{\cdot}COOH$, or $C_2H_3O{\cdot}OH$.

Acetic acid occurs in nature in the juices of many plants, especially trees, either as free acid or, generally, as the calcium or potassium salt; and, in the form of organic acetates, in the oils from many seeds. It is stated to be present in larger quantities when the plants are kept from the light. It exists in certain animal fluids; Béchamp states it to be a normal constituent of milk. Gmelin and Geiger have found it in mineral waters, doubtless from the decomposition of organic matter.

Being a very stable body both at the ordinary and at high temperatures, it is found as a product of the decomposition or destructive distillation of many organic substances. Acetic acid was first shown by Lavoisier to be formed by the oxidation of alcohol. Its true composition was ascertained by Berzelius in 1814, and Döbereiner in 1822 proved that it was formed, together with water, by the oxidation of alcohol, without the formation of carbonic acid as had been previously supposed.

Preparation.—Acetic acid is produced by the oxidation, decomposition, and destructive distillation of many organic bodies. The greater part of that used in commerce is obtained by the destructive distillation of wood.

Alcohol may be converted into acetic acid by powerful oxidising agents, such as chromic acid, nitric acid, &c. Advantage may be taken of the fact that spongy platinum or platinum black has the property of absorbing oxygen, and thus acting as a powerful oxidising agent. If spongy platinum be placed over a vessel of alcohol with free access of air, the platinum absorbs at the same time the oxygen and the alcohol vapour, which combine and produce acetic acid and water:—

$$\underset{\text{Alcohol.}}{CH_3CH_2OH} + O_2 = \underset{\text{Acetic acid.}}{CH_3COOH} + OH_2.$$

In addition to acetic acid, aldehyde (acetic aldehyde) is produced, which is intermediate in composition between alcohol and acetic acid. It is formed by the removal of two

atoms of hydrogen from the alcohol without their replacement by an atom of oxygen :—

$$\underset{\text{Alcohol.}}{CH_3{\cdot}CH_2{\cdot}OH} + O = \underset{\text{Aldehyde.}}{CH_3{\cdot}CHO} + H_2O.$$

In presence of excess of oxygen aldehyde forms acetic acid. Aldehyde is a very volatile liquid, and is liable to be lost before its conversion into acetic acid ; it is therefore necessary in all cases where acetic acid is produced by the oxidation of alcohol to allow free access of air.

This method produces a very pure acetic acid, but on account of the initial cost of the platinum (which, however, is not in any way injured by use) it is not used on the manufacturing scale.

Patents have been taken out in England for the acetification of alcoholic liquors by ozone and by nascent oxygen and also for the manufacture of acetic acid from alkali acetates by electrolysis (Plater-Syberg, Eng. Pat. 1898, 233). A French patent (360, 249, 1905) describes the preparation of acetic acid from acetylene. Acetylene is passed into a solution of a normal mercuric salt which precipitates mercury acetylide. The liquid is then boiled, when aldehyde is formed and the mercuric salt reformed. The aldehyde is then oxidised to acetic acid.

Several kinds of ferments are capable of converting fermented alcoholic liquors into acetic acid. The two chief are the *Mycoderma aceti* of Pasteur, also known as *Mycoderma vini*, 'mother of vinegar' and 'the vinegar plant,' and the *Bacterium xylinum of* Brown. Buchner and Meissenheimer have shown that the fermentation is due to enzymes in the plant-cell. They are white gelatinous nitrogenous plants, requiring for their healthy growth proteid substances and mineral salts, which are always present in wines and other alcoholic liquids. In the absence of this food they have no action on pure alcohol, but Pasteur has shown that pure alcohol, to which alkaline phosphate and ammonium phosphate have been added, is slowly acetified by this ferment, the ammonia supplying the nitrogen.

The *concentrated* or *glacial* acid is usually prepared by the distillation of a dry acetate with an equivalent quantity of strong sulphuric acid, or acid potassium or sodium sulphate.

Sodium acetate is generally used. The anhydrous salt is fused on sheet-iron pans, 6 feet by 4 feet, care being taken that no sparks reach the dried salt, as it would then ignite and burn like tinder. The mass is cooled, broken into small lumps, and distilled with concentrated sulphuric acid. The first portion distilling contains the water, the later portion is collected and cooled ; when crystals have formed the still liquid portion is removed, the crystals are melted and redistilled as before, producing the glacial acid.

When a solution of calcium chloride is mixed with a solution of calcium acetate, crystals of calcium aceto-chloride $CaC_2H_3O_2Cl, 5H_2O$ gradually separate. These crystals may be produced in comparative purity even when impure *brown* acetate of lime is used. To obtain acetic acid ordinary commercial or 'distilled' acetate of lime is mixed with the proper proportion of calcium chloride, and the solution is concentrated by evaporation until it crystallises; the mother liquor is poured from the crystals and concentrated with the production of a second crop of crystals ; this is repeated until about four crops have been produced. The crystals are dissolved in water, filtered through animal charcoal, mixed with about 10 p.c. of calcium chloride, and recrystallised, The crystals are distilled with a mixture of 1 part sulphuric acid of sp.gr. 1·84 and 2 parts water, and the acetic acid concentrated in the usual way. The glacial acid may also be prepared by the distillation of di- or acid-acetate of potash, which, when heated, decomposes into acetic acid and the normal acetate of potash. If ordinary acetic acid be heated with normal potassium acetate, the acid acetate is formed, and a weaker acid at first distils over ; as the temperature rises, the diacetate begins to decompose, and the distillate increases in strength until the glacial acid passes over. When the temperature reaches 300° the distillate becomes coloured from the decomposition of the acid (Melsens, Annalen, 52, 274 ; Compt. rend. 19, 611).

Scott and Henderson (Eng. Pat. 1896, 6711) purify the crude acetates by boiling with sodium hypochlorite until the colour is nearly gone. The solution is then cooled and allowed to settle. The clear liquid is decanted and crystallised. The crystals are of great purity. Scott (Eng. Pat. 1897, 12952) has patented a process which dispenses with lime in the manufacture of acetic acid. He distils the crude acid at 100°, and fractionally condenses the vapours. The acid collects mainly in the first portions.

Crude acetates may be decomposed with H_2SO_4 or HCl, and the acetic acid distilled *in vacuo* (Thompson, J. Soc. Chem. Ind. 1896, 357); or crude acetic acid may be treated with oxygen under pressure, filtered through charcoal and distilled over pure sodium acetate (Schmidt, Eng. Pat. 1896, 25100).

Hochstetter (J. Soc. Chem. Ind. 1902, 1469) prepares pure acetic acid by heating pure sodium acetate with dry HCl at 120°.

'Aromatic vinegar' may be prepared by distilling crystallised diacetate of copper (distilled verdigris). The acetate is dried at 160° and heated in earthenware retorts, when the glacial acid distils over. The verdigris produces about half its weight of the acid. The pleasant odour of aromatic vinegar is largely due to acetone, which is always produced when acetates of heavy metals are distilled, but camphor and essential oils are frequently added to increase or modify the smell.

Acetic acid for pharmaceutical and medicinal purposes should not decolourise a solution of potassium permanganate. To remove the organic matter which would have that effect, the acid is distilled with potassium permanganate or dichromate.

Properties.—The strongest acid solidifies at 16·7° in tabular or prismatic glistening crystals. The glacial acid may be cooled to −10° without solidification, even when agitated, but on the addition of a crystal of the acid the whole solidifies and the temperature rises to 16·7°.

The specific gravity of the crystals at 15°/4° is 1·0607 (Mendeléeff, J. 1860, 7). They melt to a mobile colourless liquid of sp.gr. 1·0543 at 16°/4° (Petterson, J. pr. Chem. [2] 24, 301), 1·0495 at 20°/4° (Brühl) which boils at 118·5° at 760 mm.

(Perkin). The liquid is uninflammable, but the vapour burns with a blue flame producing water and carbonic acid. When passed through a red-hot tube only a small portion is decomposed, producing carbon, acetone, benzene, &c. The strong acid blackens when heated with concentrated sulphuric acid, evolving sulphurous and carbonic anhydrides.

Nitric and chromic acids have no action; for this reason acetic acid is frequently used as a solvent for organic substances such as hydrocarbons, which are to be subjected to the action of chromic acid. Chlorine under the influence of sunlight replaces a portion of the hydrogen, and produces *mono-*, *di-* and *trichloracetic acids*. Similarly, bromine produces *dibromacetic acid*. On the addition of water to the glacial acid heat is evolved and the density increases until 20 p.c. of water is present; from this strength to 23 p.c. of water the density remains stationary. Further dilution lowers the density, so that either dilution or concentration from this point will produce an acid of diminished density. An acid containing only 43 p.c. of acid has the same density as the glacial acid. This, together with the slight difference between the density of acetic acid and water, renders it impossible to determine, with any precision, the percentage of acid by means of the hydrometer.

No definite hydrates of acetic acid are known (De Coppet, Ann. Chim. Phys. [7] 16, 275; Colles, Chem. Soc. Trans. 1906, 1247).

The following table shows the density of aqueous acetic acid at 15° and 20°:—

DENSITY OF AQUEOUS ACETIC ACID (OUDEMANS).

	Density			Density			Density	
p.c.	15°	20°	p.c.	15°	20°	p.c.	15°	20°
0	0·9992	0·9983	34	1·0459	1·0426	68	1·0725	1·0679
1	1·0007	0·9997	35	1·0470	1·0437	69	1·0729	1·0683
2	1·0022	1·0012	36	1·0481	1·0448	70	1·0733	1·0686
3	1·0037	1·0026	37	1·0492	1·0458	71	1·0737	1·0689
4	1·0052	1·0041	38	1·0502	1·0468	72	1·0740	1·0691
5	1·0067	1·0055	39	1·0513	1·0478	73	1·0742	1·0693
6	1·0083	1·0069	40	1·0523	1·0488	74	1·0744	1·0695
7	1·0098	1·0084	41	1·0533	1·0498	75	1·0746	1·0697
8	1·0113	1·0098	42	1·0543	1·0507	76	1·0747	1·0699
9	1·0127	1·0112	43	1·0552	1·0516	77	1·0748	1·0700
10	1·0142	1·0126	44	1·0562	1·0525	78	1·0748	1·0700
11	1·0157	1·0140	45	1·0571	1·0534	79	1·0748	1·0700
12	1·0171	1·0154	46	1·0580	1·0543	80	1·0748	1·0699
13	1·0185	1·0168	47	1·0589	1·0551	81	1·0747	1·0698
14	1·0200	1·0181	48	1·0598	1·0559	82	1·0746	1·0696
15	1·0214	1·0195	49	1·0607	1·0567	83	1·0744	1·0694
16	1·0228	1·0208	50	1·0615	1·0575	84	1·0742	1·0691
17	1·0242	1·0222	51	1·0623	1·0583	85	1·0739	1·0688
18	1·0256	1·0235	52	1·0631	1·0590	86	1·0736	1·0684
19	1·0270	1·0248	53	1·0638	1·0597	87	1·0731	1·0679
20	1·0284	1·0261	54	1·0646	1·0604	88	1·0726	1·0674
21	1·0298	1·0274	55	1·0653	1·0611	89	1·0720	1·0668
22	1·0311	1·0287	56	1·0660	1·0618	90	1·0713	1·0660
23	1·0324	1·0299	57	1·0666	1·0624	91	1·0705	1·0652
24	1·0337	1·0312	58	1·0673	1·0630	92	1·0696	1·0643
25	1·0350	1·0324	59	1·0679	1·0636	93	1·0686	1·0632
26	1·0363	1·0336	60	1·0685	1·0642	94	1·0674	1·0620
27	1·0375	1·0348	61	1·0691	1·0648	95	1·0660	1·0606
28	1·0388	1·0360	62	1·0697	1·0653	96	1·0644	1·0589
29	1·0400	1·0372	63	1·0702	1·0658	97	1·0625	1·0570
30	1·0412	1·0383	64	1·0707	1·0663	98	1·0604	1·0549
31	1·0424	1·0394	65	1·0712	1·0667	99	1·0580	1·0525
32	1·0436	1·0405	66	1·0717	1·0671	100	1·0553	1·0497
33	1·0447	1·0416	67	1·0721	1·0675			

The addition of a small quantity of water lowers the melting-point of the glacial acid considerably, as shown by the annexed table (p. 10) Dahms (Ann. Chim. Phys. [7] 18, 141).

Acetic acid is monobasic, but forms both acid and basic, as well as normal salts. It dissolves certain metallic oxides, as those of lead and copper, forming basic acetates.

It has a pungent sour taste, and when strong blisters the skin. The glacial acid has no action on litmus, but on addition of water becomes powerfully acid. It is not affected by the electric current, probably because a bad conductor, but when a little sulphuric acid is added the current decomposes it, producing, according to Renard (Ann. Chim. Phys. [5] 16, 289), carbon dioxide, carbon monoxide and oxygen. Alkaline acetates when electrolysed are decomposed into hydrogen and alkaline hydrate which

appear at the negative pole, and ethane and carbon dioxide at the positive pole.

Solidifying-point	Water to 100 parts real acetic acid	Solidifying-point	Water to 100 parts real acetic acid
°C.		°C.	
16·675	0	−3·94	16·38
16·50	0·05	−8·80	21·53
16·06	0·29	−12·80	24·56
14·54	1·15	−18·10	29·97
11·81	2·94	−17·90	30·87
7·21	6·53	−23·87	36·57
2·95	10·33	−24·90	37·52
2·46	10·74	−25·20	39·30
−2·90	15·80	−26·75	40

Acetic acid mixes with alcohol and ether in all proportions. It dissolves resins, gelatin, fibrin, albumen, essential oils, &c. Phosphorus and sulphur are somewhat soluble in the warm acid.

Acetic acid is largely used in the preparation of the acetates of copper, aluminium, iron, lead, &c.; as pyroligneous acid in calico printing; in the preparation of varnishes and colouring matters; in the laboratory and certain industries as a solvent; for domestic use; in photography; and in medicine as a local irritant and to allay fever, and in the form of smelling salts.

Analysis.—Commercial glacial acid should contain at least 97 p.c. of absolute acid. If 9 volumes oil of turpentine be agitated with 1 volume of acid, no turbidity will be produced if the acid contain 97 p.c. or upwards. Acid of 99·5 p.c. produces no turbidity with any proportion of turpentine (Bardy, Chem. News, 40, 78).

A very delicate test for the presence of water is to mix the acid with an equal bulk of carbon disulphide in a dry tube, and warm with the hand for a few minutes; in presence of a trace of water the liquid becomes turbid.

The commercial acid may contain sulphuric acid, sulphates, sulphurous acid, hydrochloric acid, chlorides, arsenic (derived from sulphuric acid), and copper, lead, zinc, and tin derived from the vessels used in the manufacture.

The presence of sulphuric acid or sulphates is shown by the production of a white precipitate with barium chloride. To the filtered solution bromine or chlorine water is added, producing, if sulphurous acid be present, a further precipitate of barium sulphate. Hydrochloric acid and chlorides are detected and estimated with silver nitrate.

In testing for metals a considerable bulk of the acid should be evaporated; a few drops of hydrochloric acid are added, and a current of sulphuretted hydrogen passed through the liquid; a black or brown colouration or precipitate indicates lead or copper. Copper may also be detected in the evaporated liquid by the brown precipitate produced on the addition of potassium ferrocyanide, and estimated by electro-deposition. To test for zinc, the solution, after the passage of sulphuretted hydrogen, is filtered, nearly neutralised with ammonia, and sodium acetate added, when zinc will be precipitated as white sulphide. For arsenic Reinsch's or the electrolytic test may be used.

Small quantities of acetic acid may be recognised by neutralising with caustic potash, adding arsenious oxide, evaporating to dryness, and heating, when the characteristic smell of cacodyl is evolved.

To determine the free acetic acid in a solution it is usual to titrate a weighed quantity with caustic soda standardised with acetic acid of known strength, or of acid potassium tartrate (Stillwell and Gladding).

As indicator litmus may be used, but as it is rendered blue by the normal sodium acetate, it is preferable to use phenol-phthalein, to which that substance is neutral; this is also more sensitive, and, where coloured, the liquid may be considerably diluted without impairing the delicacy of the reaction.

To estimate small percentages of water in acetic acid, the solidifying-point may be determined and the percentage found by the table before given.

For the separation and estimation of formic, acetic, propionic, and butyric acids see Zeit. Anal. Chem. 1899, 38, 217. Chapman (Analyst, 1899, 24, 114) describes a method for the estimation of *iso*valeric acid in acetic acid.

The acetic acid in acetates may be determined by distilling about 1 gram of the salt nearly to dryness with 10 c.c. of a 40 p.c. solution of phosphoric acid (free from nitric and other volatile acids); water is added and the distillation repeated to remove the last traces of acetic acid; the distillates are mixed and titrated as above with standard alkali. This method of distillation may also be used for highly coloured solutions of acetic acid where direct titration is inadmissible.

Preparation of Vinegar.

In all processes for the manufacture of vinegar advantage is taken of the oxidising action of the vinegar fungus already described; the souring of wines and other alcoholic liquids is due to this organism, the germs of which are always present in the air, and are deposited and grow in any suitable medium.

The action is more rapid when the liquid is rich in vegetable matter and poor in alcohol, and when the surface exposed to the air is large. The precentage of alcohol should not, however, be too low; the acetous fermentation proceeds but slowly in a liquid containing less than 3 p.c. alcohol.

Wine vinegar. (Fr. *Vinaigre*; Ger. *Weinessig.*) In the wine district of Orleans, wines which have become sour are generally used for the preparation of vinegar. For this purpose full-bodied wines are preferred. If they contain above 10 p.c. alcohol they are suitably diluted with weaker wines. The wine, before being fermented, is usually left for some time in contact with beech shavings, on which the lees are deposited, rendering the wine brighter. A certain amount of extractive matter is, however, necessary for the proper growth of the plant, and if the wine be old and the matter deposited, the fermentation is much retarded. Wine one year old is preferred.

The 'Vinaigrerie' is usually a building of southern aspect; the rooms in which the

process is conducted are low-roofed, and the walls are provided with openings for the admission of air, which can be closed when the temperature is not sufficiently high.

A number of casks of well-seasoned oak, bound with iron hoops, each holding from 50 to 100 gallons are supported on their sides in rows about 18 inches from the floor, one set being frequently placed above another, in which case those nearest the roof are found to work most rapidly. Each cask is bored with two holes in the front end, a larger one, the 'eye,' for the addition of wine or the removal of vinegar, and a small one for the admission of air.

When first used the casks are thoroughly scalded with boiling water to remove extractive matter, one-third filled with boiling strong vinegar, and allowed to stand for eight days; from that time wine is added in charges of about 10 pints every eight days until not more than two-thirds full; after a further interval of 14 days a portion, varying from 10 gallons to half the total bulk, is drawn off and the periodical addition of the wine continued. The temperature of the chambers should be about 25°, and is kept up when necessary with a stove. In order to ascertain if the fermentation is completed at the end of the usual time, the workman plunges a white spatula into the liquid; if a reddish froth adheres, more wine is added and the temperature raised; a white froth indicates the completion of the process. More than eight days is sometimes required to complete the oxidation, in which case stronger wine and a higher temperature may be used. The sluggishness may, however, be due to the casks becoming foul, which occurs usually after about six years' working. The deposit of argol, yeast sediment, &c., is thoroughly removed, the casks cleansed and recharged with hot vinegar as in the case of new casks. Good casks will often last twenty-five years.

When working satisfactorily each cask will produce about twice its capacity of vinegar annually.

Before storing, the vinegar is usually passed through the 'rapes' where it is 'brightened' and the acetification completed.

In other parts of France and in Holland and on the Rhine the following method is used. The wine is placed in two large upright tuns about 9 feet high and 4 feet wide, open to the air. Each tun has a perforated false bottom about 12 inches above the true bottom; on this is placed a quantity of vine cuttings, stalks, &c., so as to expose a large surface for the formation of the fungus. One of the vats is half, and the other completely, filled. The acetification progresses more rapidly in the former; this, after twenty-four hours, is filled from the full cask, in which the action then increases. This alternate transference is continued daily until the acetification is complete. The most favourable temperature is about 24°. The vinegar is run off into casks containing chips of birch wood on which the lees settle, and in about fourteen days being thus clarified is stored in close casks for the market.

Malt vinegar. *Malzgetreide Bieressig. Acetum Britannicum.* This is prepared from an infusion of malt which has first been fermented to produce alcohol. Six bushels of crushed malt are extracted three times with water, in a circular mash tun supplied with a central stirrer, the first extraction with water at 72°, the second at a higher temperature, and the third with boiling water. The extracts, which together should not exceed 100 gallons, are passed into a large cast-iron tank 24 feet by 8 feet, cooled by refrigerators to 24°, poured into a large circular vessel, mixed with 3 or 4 gallons of good yeast and fermented briskly for about forty hours. The extract is filtered, and, where intended for the manufacture of the best keeping vinegar, is stored in casks for some months, whereby the extractive matters which would induce putrefaction are deposited.

This 'wash' may be treated by the 'quick vinegar process' or acetified in large casks lying on their sides in a room at a temperature of about 24°. The bung-holes of the casks are open, and at each end near the top an opening is made for the circulation of air. When conducted in the open air the process is known as 'fielding'; from eight to twenty rows of casks constitute a vinegar field. The operation is commenced in the spring and completed in about three months.

The fermenting casks are frequently worked in pairs; one being completely and the other three parts filled, acetification progresses more rapidly in the latter; every day a portion is transferred thereto from the full cask, being replaced by an equal amount of the more fermented liquid, until completed.

Before storing, it is necessary to filter the vinegar from the extractive matter. The filtering vessel, 'rape' or 'fining tun,' is a large cask, usually wider at the base than at the top, fitted with a false bottom, above which it is filled with spent tanner's wood, wood shavings, or, which is far preferable, with 'rapes,' the pressed cake of residue from the British wine manufacture, consisting of the stalks and skins of grapes and raisins. Through this the vinegar is poured, escaping through a tap beneath the false bottom into a tank from which it is continuously pumped to the top of the vessel and again passed through until the last traces of alcohol have been oxidised and the vinegar cleared and brightened. In this way pickling vinegar is produced.

For household vinegar, the malt is acetified in upright casks fitted with false perforated bottoms covered with a layer of rapes; after twenty-four hours it is transferred to another similar cask, remaining there for two or three days, and thence to a third and fourth cask. A portion of the liquid is transferred to the 'mothers' and the remainder allowed to ferment. A little argol is occasionally added to produce a flavour of wine vinegar, the liquid being clarified with isinglass.

Vinegar casks are made in three sizes, holding 25, 50, and 116 gallons.

Quick vinegar process. *Schnellessigbereitung.* This method, applicable to any alcoholic liquid, is founded on that proposed in 1720 by Boerhaave, and was first introduced by Schutzenbach in 1823. It differs from the other processes in causing the liquid to expose a very large surface to the action of the air, one gallon being sometimes made to cover a surface of 100 square yards.

The vat is usually from 6 to 12 feet high, and from 3 to 4 feet wide. In England it is frequently as much as 13 feet high, 14 feet wide at the top, and 15 feet wide at the base. At a distance of 18 inches from the bottom, six or more air holes are bored 1 inch in diameter, inclining downwards towards the inside; just above these a false perforated bottom is fixed. A quantity of beechwood shavings is thoroughly washed with hot water, dried and placed on the false bottom, nearly filling the vat. The shavings may be substituted with advantage by pieces of charcoal about the size of a walnut, from which the saline particles have been removed by acid and subsequent washing. The acetifying action is assisted by the power of absorbing oxygen possessed by the charcoal.

Near the top of the tun is fixed a wooden disc perforated by holes as large as a quill, about 1 inch apart; through these, twists of cotton yarn or string are passed, of sufficient length to touch the shavings: they are tied into knots at the upper end to prevent them from slipping through. There are also five or six larger holes through which pass glass draught tubes projecting on either side of the disc, 1 to 2¼ inches wide and 4 to 6 inches long, firmly fastened so that no liquid can pass round them through the hole.

About 1 inch from the true bottom is fixed a bent tube attached to a tap through which the vinegar is drawn as soon as it rises to a height of about 15 inches. The vessel is closed with a tightly-fitting lid through which a circular opening is cut for the admission of liquid and for the escape of air.

Before commencing the fermentation it is necessary to 'sour' the shavings; for this purpose hot vinegar is poured in from the top and allowed to soak for at least twenty-four hours.

The composition of the fluid used varies considerably: any alcoholic liquid may be used, but the presence of a trace of tarry matter, such as is present in pyroligneous acid, prevents the action. According to Wagner (Chem. Technology), the following mixture is generally used: —4½ gals. (20 litres) brandy of 50°Tralles (42·5 p.c. by weight), 9 gals. vinegar, and 27 gals. water, to which is added a mixture of bran and rye to promote the growth of the vinegar fungus.

Another standard liquor is 50 gals. brandy or whisky 52 p.c. by weight, 37 gals. beer or malt wort with about $\frac{1}{1000}$ part of ferment; this is mixed with 3 to 4 vols. of soft water before passing through the tuns. Molasses or honey in the proportion of 2 lbs. to 50 gals. is sometimes added, to produce a more finely coloured vinegar.

For 'wine malt,' 40 lbs. wheat-meal and 80 lbs. barley-meal are ground, and mixed together with 40 gals. warm water (50°); after settling, the clear liquid is drawn off, the residues are treated with hotter water (70°), settled, the liquid removed and the residue again treated, this time with boiling or nearly boiling water, in such quantity that the total washings amount to about 100 gals. The solution is cooled, mixed with 15 lbs. yeast, and allowed to ferment at 27° for five or six days; it is then known as the 'gyle.' The temperature of the chamber being about 38° the liquid which, where the 'generator' or 'graduator' is new, is heated to 50°, or, where in use for some time and thus in good condition, to 25°, is poured over the upper disc and trickles slowly down the twisted threads, which swell and prevent too rapid passage. As the liquid flows over the shavings it becomes oxidised, the action being more rapid when, after some time in use, the shavings have become coated with the 'mother of vinegar.' When the action is satisfactory the temperature of the interior rises on account of the oxidation to 37°, and creates a constant upward current of air which passes from the openings below the false bottom, round the shavings and through the tubes in the upper disc.

When the liquid contains no more than 4 p.c. alcohol, the vinegar which collects is entirely acetified, but where a stronger liquid is used it may be necessary to pass it three or four times through the graduator. When a strong vinegar is required, that produced from one of the above-mentioned liquids is mixed with a more alcoholic liquid, and again passed through, and this may be repeated until 1 oz. of the liquid will neutralise sixty grains pure dry potassium carbonate, corresponding to about 12 p.c. acetic acid by weight. Each graduator will contain about 80 gals. of liquid and will produce daily 15 gals. of good vinegar. One workman usually attends to ten tuns.

By this process, on account of the large surface exposed, a considerable loss of alcohol, and hence of acetic acid, is unavoidable, amounting when properly carried out to about 6 p.c. of the whole; but if the temperature has been allowed to rise too high, the loss is greatly increased. At the same time sufficient air must be introduced to convert the alcohol directly into acetic acid, or the loss will be further increased by the formation of the volatile aldehyde.

By some makers the vapours from the tuns are passed over or through water to absorb the alcohol and aldehyde. For this purpose two floating gasometers are sometimes used: one rises and removes the air which has performed its work, while the other falls, keeping up a constant current of air through the generator. As each gas-holder falls it discharges the air through a cistern of water, which absorbs the volatile products and is used for the preparation of a further quantity of malt extract.

Recent improvements in the quick vinegar process have taken the form of labour-saving contrivances and of devices to avoid loss by evaporation. Leaker has patented a process whereby the acetification takes place in closed rectangular vessels containing shelves of absorbent woven material. To the vessel is attached a condensing worm into which the vapours are drawn by a fan.

About one-third of the total extractive matter in the malt is lost or dissipated in the fermentation and acetification.

In Singer's generator a number of vessels are placed one above another in a shed in which a suitable temperature is maintained and from which draughts are excluded. The vessels are connected together by wooden tubes provided with longitudinal slits through which air can pass. The liquid slowly drops through the tubes from one vessel to another, and, exposing a large surface to the air, becomes acetified. It is stated that the loss of alcohol usually experienced is avoided in this process. In many vinegar works the larvæ of the 'vinegar fly'

(*Drosophila cellaris*) and 'vinegar eels' (*Anguillula aceti*) abound.

Vinegar is found occasionally to decompose when shaken, probably on account of the lees becoming mixed with the liquid.

Of late years delicacy and uniformity of flavour in the various kinds of vinegars have been obtained by the use in acetification of pure cultures of the particular bacterium (Henneberg, Zeit. für Spiritusind, 1898, 180, and Cent. Bakt. 1905, 14, 681; Rothenbach, Woch. für Brau. 15, 445, and Deut. Essiggind, 1905, 9,217, and Woch. für Brau. 1906, 23, 260; Mayer, Zeit. für Spiritusind, 21, 334; Büchner and Gaunt, Annalen, 1906, 349, 140).

In addition to wine and malt, vinegar is prepared from many other substances. *Cider vinegar* is of a yellowish colour, sp.gr. 1·013 to 1·015. It contains 3½ to 6 p.c. acetic acid, and on evaporation leaves a mucilaginous residue, smelling and tasting of baked apples, and containing malic but not tartaric acid. The residue varies from 1·5 to 1·8 p.c. Genuine cider vinegar is distinguished from spurious cider vinegar by the residue, which consists of glycerol, albuminous matters, gums, malic and other organic acids and mineral matters. They have no rotation and little cupric reducing power after the usual clarification with basic lead acetate solution. The ash of a pure cider vinegar amounts to not less than 0·25 p.c., consisting mainly of potash, with small quantities of alumina, lime, magnesia, sulphate, and phosphate, variable amounts of carbonate, and complete absence of soda. Spurious cider vinegars have a molasses-like residue and an ash with a large percentage of lime or soda (Doolittle and Hess. *See* also Smith, J. Amer. Chem. Soc. 1898, 20, 3; Leach and Lythgoe, *l.c.* 1904, 26, 375; Van Slyke, New York Agric. Exp. Stn. Bull. 1904, 258, 439; Ladd, N. Dakota Exp. Stn. Bull. 32, 278). *Perry* and *crab-apple vinegars* are used in Wales and Monmouthshire, and possess characteristic properties.

Ale vinegar is prepared from sour strong pale ale. It usually gives a large residue (5 to 6 p.c.), and is very liable to decomposition. *Crystal vinegar* is ordinary vinegar decolourised by filtration through animal charcoal. A household vinegar is made in Germany from 7½ gals. soft water, 2 lbs. honey or brown sugar, 1 gal. whisky or corn spirit, 2 ozs. cream of tartar.

Glucose or *sugar vinegar* is prepared by the conversion of amylaceous substances into sugar, by the action of dilute acids, followed by fermentation and acetification. It contains glucose, dextrin, and very often gypsum, with hardly any proteins. The ash is composed mainly of potassium salts, is rich in sulphates, and in the case of cane-sugar vinegars, readily fusible (Allen's Comm. Org. Anal. 1909, 498). It is stated to be used for adulterating wine vinegar. It can be distinguished from other vinegars by the addition of 3 or 4 volumes strong alcohol, which produces a slimy precipitate of dextrin. Barium chloride usually gives a copious precipitate, due to the sulphuric acid used in the manufacture of the glucose.

Vinegar is now made from skim milk by addition of sugar, neutralisation with chalk, pitching first with yeast and then with *Mycoderma aceti* (Barbier Fr. Pat. 1903, 334071).

An artificial vinegar is made by mixing acetic acid with water and adding burnt sugar (caramel) and acetic ester to produce the proper colour, odour, and taste. This vinegar differs from genuine kinds by the absence in the evaporated residue of phosphoric, tartaric, or malic acid.

Properties.—Malt vinegar is a brown liquid of a characteristic odour due to the presence, in addition to the acetic acid, of acetic and other esters. Acetic ester is frequently added in small quantity to increase this aroma.

The vinegar of the B.P. has a sp.gr. of 1·017 to 1·019. In commerce it usually occurs in four strengths, numbered 18, 20, 22, and 24. The last is 'proof' vinegar; it contains 6 p.c. acetic acid, and its sp.gr. is 1·019. The numbers denote the fact that one fluid ounce of the liquid will neutralise 18, 20, 22, and 24 grains respectively of pure dry sodium carbonate. The real weight of acetic acid in one ounce of liquid may be found by multiplying its number by 1·132, and the percentage by weight by multiplying the number by 0·259. Thus No. 24 should contain 6·22 p.c. of absolute acetic acid.

The addition of 1 part sulphuric acid to 1000 parts vinegar is lawful, and is occasionally made, though the idea that it prevents decomposition has been shown to be erroneous.

Malt vinegar usually contains alcohol, gum, sugar, and extractive matter, acetates, chlorides, free and combined sulphuric acid, and on evaporation and ignition leaves a residue containing much phosphate.

Wine vinegar varies in colour from pale yellow to red; that made from white wine is most esteemed; it usually has an alcoholic odour. Its sp.gr. is 1·014 to 1·022; it contains from 6 to 12 p.c. acetic acid. A litre (1·76 pint) of Orleans vinegar usually saturates 6 or 7 grams (92 to 108 grains) of pure dry sodium carbonate. On evaporation the total extract varies from 1·7 to 2·4 p.c., of which 0·25 p.c. is usually potassium tartrate, a salt peculiar to wine vinegar. The residue, with the exception of the tartar, should dissolve in alcohol.

The proof vinegars of various countries differ considerably; the minimum of acetic acid allowed by the various Pharmacopœias is—France, 8 to 9 p.c.; England, Germany, and Austria, 6 p.c.; Belgium, 5·6 p.c.; Russia, 5 p.c.; United States, 4·6 p.c. Genuine vinegar seldom falls below 5 p.c., and should be condemned as adulterated with water when the amount is as low as 3 p.c.

Analysis of Vinegar.

The adulterants to be looked for in vinegar are mineral acids, especially sulphuric acid, more rarely hydrochloric, and still more rarely nitric acid, tartaric acid, and pyroligneous acid; flavouring agents, cayenne, ginger, &c.; metals—usually derived from the vessels used—copper, lead, zinc, tin, arsenic (from sulphuric acid).

The presence of free mineral acids may be detected by the addition of Paris violet (methylaniline violet). Prepare a solution of this dye by dissolving 1 part in 1000 parts water, and add two or three drops of the solution to about one ounce of the vinegar. In presence of 1 p.c. free mineral acid the colour is green, with 0·5 p.c. bluish-green, and with 0·2 p.c. blue (Hilger, Arch. Pharm. 1876, 193).

If mineral acids are added to vinegar in small quantity they liberate an equivalent amount of acetic acid from the acetates, until the acetates are wholly decomposed, and form salts with the base, thus ceasing to exist as free acids. As acetates on ignition produce carbonates, the presence of an alkaline reaction in the ash indicates the presence of acetates in the vinegar, and therefore the absence of free mineral acids, though these may have been added in small quantities in the first instance. If, however, the ash be neutral, the presence of mineral acids is indicated. Hydrochloric acid may be tested for by adding silver nitrate to the distillate from the vinegar.

Heavy metals may be considered absent if no darkening is produced on passing sulphuretted hydrogen for some time through the solution. To determine the acetic acid in vinegar 110 c.c. may be distilled until 100 c.c. have passed over. The 100 c.c. will contain four-fifths of the total acid, and may be titrated with standard alkali and phenolphthaleïn, making an allowance for the one-fifth left in the retort.

Formic acid may be estimated by the method recommended by Ost and Klein (Chem. Zeit. 1908, 32, 815). The acid is neutralised with alkali and titrated with permanganate. Other substances which reduce permanganate must be absent.

Oxalic acid may be estimated by concentrating the vinegar and then boiling with calcium acetate solution.

Potassium hydrogen tartrate is estimated by titration against $N/2$ alkali, and tartaric acid by conversion to potassium hydrogen tartrate and subsequent titration (Zeitsch. anal. Chem. 1908, 47, 57).

(For the estimation of methyl alcohol in vinegar, *see* Ann. Chim. anal. 1901, 6, 127 and 171.)

Cayenne pepper, ginger, and other flavouring matters may be discovered by neutralising the vinegar and tasting.

Chevallier has found fuchsine in French wine vinegars.

Metallic Acetates.

Aluminium acetates.

The triacetate or normal acetate $Al_2(C_2H_3O_2)_6$ is not known. A solution corresponding to this compound, but which appears to be a mixture of the diacetate and acetic acid, is the only acetate of commercial importance. It is known as 'red liquor' or 'mordant rouge,' and is largely used in dyeing and calico-printing, especially for the production of red colours, madder reds and pinks (whence its name of red liquor); for the production of dense lakes, and for waterproofing woollen fabrics. It is prepared by several methods.

A solution of alum is added to acetate of lime liquor. The lime is precipitated as sulphate, its place being taken by the aluminium forming aluminium acetate; sulphate of ammonia or potash (according to whether ammonia or potash alum has been used) is produced at the same time. The mixture is agitated and allowed to settle, and a small quantity of the clear fluid removed and tested by the addition of alum; if a precipitate forms sufficient alum has not been used and more must be added. The solution is filtered and concentrated to a specific gravity of 1·087 to 1·10 and allowed to deposit any sulphate of lime still present. Sulphate of lime, being slightly soluble in water, is contained in the liquid in small quantity, and diminishes the brilliancy of the colours produced. By the substitution of lead acetate for the calcium acetate a better product is obtained. For this purpose 100 lbs. alum is dissolved in 50 gallons water, and treated with 100 lbs. finely-powdered lead acetate with constant stirring: or, using the same quantities, 10 lbs. crystallised carbonate of soda is added before the acetate of lead; or, to 100 lbs. alum in 50 gallons water 6 lbs. of carbonate are added in small portions followed by 50 lbs. of lead acetate. The addition of the carbonate is made with a view to the production of a basic sulphate of alumina as well as the acetate, and as the sulphate assists the mordanting, less acetate is required. The solutions are allowed to settle and decanted. They contain the aluminium acetate mixed with basic aluminium sulphate and alkaline sulphate.

An aluminium sulpho-acetate appears to act satisfactorily. It is prepared by mixing (1) 453 lbs. ammonia alum (or 383 lbs. aluminium sulphate), 379 lbs. lead acetate, 1132 lbs. water; or (2) 453 lbs. alum (or 333 lbs. aluminium sulphate) and 158 lbs. acetate of lime. The mixture is agitated, settled, and the clear liquid decanted.

By the use of aluminium sulphate, red liquor of the same density contains much more of the active alumina than that prepared with alum. Thus in a sample of the former 1 gallon contained 4 oz. 416 grs. alumina whilst the average amount found in three samples prepared from alum was 3 oz. 245 grs. The addition of a little ammonia or other alkali to the red liquor prepared from aluminium sulphate is advantageous for certain colours. Red liquor usually contains from 3 to 5 p.c. alumina (Al_2O_3) and 6 to 10 p.c. acetic acid; its density varies from 1·085 to 1·120.

Ammonium acetate $C_2H_3O_2NH_4$.

The crystalline salt is usually prepared by saturating glacial acetic acid with dry ammonia gas. In solution it may be prepared more cheaply by neutralising acetic acid solution with ammonia. On evaporation, a solution of the salt loses ammonia, and leaves the acid acetate or diacetate.

Ordinary solid ammonium acetate always has an odour of acetic acid; it is very soluble in water and alcohol.

Pure ammonium acetate should be entirely volatilised on heating. The commercial salt usually contains the same impurities as sodium acetate.

Calcium acetate. *Diacetate of lime. Pyro lignite of lime.* $Ca(C_2H_3O_2)_2$.

This important salt is prepared by neutralising acetic acid, or pyroligneous acid, with lime or chalk.

In the preparation from pyroligneous acid, the crude acid may be used in which case the acetate of lime is known as *brown acetate*; or the distilled liquor may be employed, producing *grey acetate*. The acid is placed in large wooden or iron pans, and powdered chalk or lime added in slight excess; the liquor remains at rest at a warm temperature until settled, and is then siphoned off into the evaporating pans. It is generally evaporated by coils of pipe through

which steam passes; in this case the vessels are usually wooden, and lined with lead, but sometimes iron pans are used, the evaporation being conducted over a fire. As the liquid evaporates, tarry impurities rise to the surface, and are removed with a skimmer. As the acetate forms, it is withdrawn and drained in wicker baskets suspended over the pans.

The proper drying of the salt is necessary to the formation of a good product. In large works a drying house is used, which is usually a wind furnace 7 or 8 feet long, 4½ feet broad. It is first heated from 75° to 115°, and the fire slackened; the salt is then spread over the bottom to the depth of about 2 inches, and when somewhat dry an equal quantity is spread above it, the salt is repeatedly turned, and the heat continued for about 24 hours. When apparently dry, the heat is increased to about 125°, and the last traces of moisture driven off. Care must be taken that the heat is not too high, or the salt becomes decomposed. As in the case of sodium acetate, no sparks must touch the mass, or it may burn away like tinder.

The product, when prepared from the *brown* liquor, is dark-coloured and contains charcoal and decomposed tarry matters; it may be dissolved in 3 parts hot water, filtered through animal charcoal, and again evaporated and crystallised yielding a nearly colourless product.

Pure calcium acetate crystallises in silky needles or prisms containing two molecules of water. At the ordinary temperature the crystals effloresce, and at 100° become anhydrous, forming a white powder of saline taste, very soluble in water.

Calcium acetate is used in the preparation of other acetates, and of acetic acid, and in calico-printing. The pure salt is completely soluble in water and proof spirit. The commercial article usually contains 62 to 67 p.c. of real acetate, and 1 to 8 p.c. of matters insoluble in water. The impurities are hydrate, carbonate, and sulphate of lime and tarry matters; formate and other salts of lime with fatty acids also occur.

Many methods of assay for this substance are in use, varying considerably in accuracy.

The most trustworthy method is to distil with pure phosphoric acid and titrate the distillate as already described under acetic acid (*see* Stillwell, J. Soc. Chem. Ind. 1904, 305; Grosvenor, *ibid.* 530; Gladding, J. Ind. Eng. Chem. 1909, 250).

Calcium aceto-chloride $CaC_2H_3O_2Cl,5H_2O$ has already been described as used in Condy's process for the preparation of pure acetic acid.

Copper acetates.

The normal *copper acetate* is prepared by dissolving cupric oxide or verdigris in acetic acid; or by the action of copper sulphate on the acetates of lead, calcium, or barium.

It crystallises in prisms; soluble in 13 parts cold or 5 parts hot water, and in 14 parts alcohol. In commerce it usually occurs in bunches of deep-green coloured opaque crystals known as 'grappes.'

Copper acetate is used in the manufacture of pigments; as an oxidising agent in the indigo vat; and, to a slight extent, for the preparation of acetic acid.

Basic copper acetate. *Verdigris. Vert-de-gris. Vert de Montpellier. Grünspan.*

This substance consists of a mixture of mono-, di-, and tri-basic acetates of copper, which are present in different proportions in different varieties of verdigris.

At Grenoble and Montpellier the following process is used: The 'marcs' or residues from the wine factories, consisting of the skins and stems of grapes, are loosely placed in earthen vessels, about 16 inches high, 14 inches in diameter at the widest part, and 12 inches at the mouth, covered and allowed to ferment, until on inserting a piece of copper (previously moistened with verdigris and dried), it becomes uniformly coated green in 24 hours. The fermentation should not proceed too far, or decomposition may ensue.

The copper used is in sheets $\frac{1}{24}$ inch thick, 4 to 6 inches long, and 3 to 4 broad, each weighing about 4 oz.; they are freed from scales, if necessary, rubbed with a solution of verdigris and dried; unless this precaution be adopted, the first coating produced by the marcs will be black instead of green. They are heated over a charcoal fire until as hot as the hand can bear, and placed in an earthenware vessel in layers with the marcs. 30 to 40 lbs. of copper are used for each vessel. In from ten to twenty days, according to the temperature, the covers are removed, when, if the process has progressed favourably, the marcs will be whitish and the copper covered with fine, glossy, green crystals. The plates are then removed and placed on end one against another. After two or three days they are moistened by immersion in water or damaged wine, and again placed on end for about a week. This alternate moistening and exposure to the air is continued for about six or eight weeks. The plates thus become covered with increasing coatings of the verdigris, which is detached and the plates are again used until entirely eaten away. The verdigris is kneaded with a little water into leather bags, pressed into rectangular cakes and dried.

This substance is known as *blue verdigris*, and consists principally of the basic acetate

$$(C_2H_3O_2)_2Cu_2O.$$

It should be dry, of a fine bluish colour, and soluble in dilute acids and ammonia.

Green verdigris contains as a principal constituent the sesquibasic acetate, $CuO{\cdot}2Cu(C_2H_3O_2)_2$, and is prepared by placing the copper plates alternately with cloths moistened every two or three days with pyroligneous acid or acetic acid until the plates show green crystals. The plates are arranged so as to allow free access of air and occasionally moistened, for five or six weeks. Large quantities of verdigris are manufactured in England by this process from pyroligneous acid. The imports of verdigris are very small.

The various forms of verdigris are used as oil and water colours. With white lead it is used in Russia and Holland as an oil paint, which by double decomposition produces a peculiar green. The paint is considered a good preservative. Verdigris is used in dyeing and calico-printing, and for the preparation of Schweinfurth green and other copper paints.

Verdigris is frequently adulterated with chalk, sand, clay, pumice, and sulphates of copper, barium, and calcium. When brass sheets have

been used in the preparation instead of copper, zinc will also be present.

When warmed with dilute hydrochloric acid the sand, clay, baryta, &c., will remain undissolved, and may be weighed. The total residue in a good sample will usually amount to 3 p.c., but should not exceed 6 p.c.

Aceto-arsenite of copper. *Schweinfurth green* (*v.* ARSENIC).

Ferric acetate $Fe_2(C_2H_3O_2)_6$. This salt is prepared by the addition of calcium or lead acetate to ferric sulphate or iron alum, avoiding excess of the acetate. It is used as a mordant, its action corresponding with that of aluminium acetate. An alcoholic solution is used in medicine.

For many purposes a mixture of ferrous and ferric acetates is preferred. It is prepared by repeatedly pouring pyroligneous acid on iron turnings until saturated with iron. The liquid is known at 'pyrolignite of iron,' 'bouillon noir,' 'liqueur de ferraille.'

Ferrous acetate $Fe(C_2H_3O_2)_2$. *Pyrolignite of iron; iron liquor or black liquor.* Is prepared on the large scale by the action of crude pyroligneous acid of sp.gr. 1·035 to 1·040 on iron turnings, nails, &c., at a temperature of 65°. The solution is frequently agitated and the tarry matters skimmed from the surface as they rise.

It is found that the purified acid produces a less satisfactory liquor, a fact due, according to Moyret (J. Soc. Dyers, i. 117), to the presence of a small quantity of pyrocatechol in the crude acid, which forms a compound with the ferrosoferric oxide in the solution, and causes its intense colour and keeping properties.

The liquid is intensely black, of sp.gr. 1·085 to 1·090, and is evaporated until its density rises to 1·120, or sometimes to 1·140. It is then ready for use, and is known as 'printer's iron liquor.' The liquor of density 1·120 contains about 10 p.c. iron.

The density of the liquor used by dyers is frequently raised by the addition of copperas (ferrous sulphate); thus, the addition to 1 gallon of black liquor, sp.gr. 1·085, of ½ lb. copperas, would raise its density to 1·111. Tannin also is sometimes added.

Black liquor is also prepared by the action of ferrous sulphate on acetate of lime; the liquor produced has an average density of 1·11, and always contains sulphate of lime. By the action of lead acetate on ferrous carbonate, carbonate of lead and ferrous acetate are produced.

Black liquor absorbs oxygen from the air, forming ferric acetate, which is always present in the liquid. To diminish this action clean metallic iron is frequently added.

It is largely used in calico-printing and in dyeing, in the preparation of blue, violet, black, brown, and other colours, and for producing a black colour on hats, furs, leather, wood, &c.

Lead acetate. *Normal or di-acetate of lead. Sugar of lead. Sel de Saturne. Bleizucker.* $Pb(C_2H_3O_2)_2$.

For the preparation of *white acetate* of lead, leaden vessels are used, or copper pans, on the bottom of each of which a piece of metallic lead is soldered to produce a galvanic action and prevent the copper from being acted upon. In the vessel acetic acid of 45 p.c. or less is placed, and to 100 parts of 45 p.c., or a proportionate quantity of a weaker acid, 86·5 parts of litharge are added in small quantities, with constant stirring, until the liquid is nearly neutral; it is then heated to boiling and impurities skimmed from the surface, transferred to another vessel and evaporated to a density of 1·5, and removed to the crystallising pans, which are usually of wood, lined with lead or copper, 4 feet by 2 feet, and 6 or 8 inches high. The coarsely crystalline mass thus obtained is drained on wooden racks, and broken into lumps for the market.

A coarser variety, known as *brown acetate*, is prepared by substituting distilled pyroligneous acid for the purer acid. The muddy liquid produced is settled in a large tun, and the supernatant liquid transferred to a large iron pan and heated to boiling. It is again allowed to settle, transferred to another pan, evaporated until crystallisation commences, and about 3 volumes of water added, causing the remaining impurities to rise to the surface. The liquid is skimmed and diluted if the liquid is not sufficiently clear, and again evaporated until a small portion of the liquid crystallises on removing and cooling. It is then ladled into pans and allowed to crystallise.

As a rule, about 3 parts acetate are produced from 2 parts litharge.

By another method granulated lead, white lead residues, &c., are placed in vessels standing obliquely one above another; the upper vessel is filled with strong acetic acid, which after the expiration of half an hour is allowed to run into the second vessel. Every half-hour it is removed to a lower one. After the acid has been removed, the lead absorbs oxygen rapidly, and becomes heated. On leaving the last vessel, the acid is again passed through the series, dissolving the acetate which has been formed, and is evaporated and crystallised.

Schmidt (*Eng.* Pat. 1897, 7192) describes a process for preparing the neutral and basic acetates of metals such as lead and copper by the action of dilute acetic acid and oxygen upon the metal contained in closed iron cylinders.

Pure lead acetate is a white crystalline salt of sweetish taste and weak acid reaction, containing 3 molecules of water. It dissolves in 1·5 parts cold water, and in 0·5 hot water. At 280° it melts, and when heated more strongly it forms a basic salt and suddenly solidifies.

Lead acetate is largely used in dyeing and calico-printing; for the preparation of alum mordants, &c.; in the manufacture of chrome yellow and other pigments, and in medicine.

Lead forms two well-defined basic acetates —the dibasic acetate $Pb(C_2H_3O_2)_2PbO,2H_2O$ (Wittstein, *Annalen*, 52, 253), formed by dissolving litharge in the normal acetate in calculated proportions; and the tribasic acetate $Pb(C_2H_3O_2)_2 2PbO\cdot aq$, prepared by boiling the normal acetate with excess of litharge for some time. Solutions of subacetate of lead are used in medicine as *Goulard water* and *Liquor plumbi subacetatis.*

Magnesium acetate. A basic acetate of magnesia, prepared by warming the normal acetate with magnesia, is stated to be a powerful antiseptic, disinfectant, and deodoriser (W. Kubel, Ber. 15, 684 686). A syrupy solution of the salt containing suspended magnesium hydroxide is found in commerce under the name of 'Sinodor.'

Potassium acetate $C_2H_3O_2K$ occurs in the sap of many plants, and of trees.

Its mode of preparation is similar to that of sodium acetate. It is a deliquescent crystalline solid, soluble in 0·53 part ice-cold water, and in hot water forms a solution which, boiling at 169°, contains 88 p.c. of the salt.

When chlorine gas is passed through a solution of potassium acetate, carbonic acid is evolved and a powerful, unstable, bleaching fluid is produced.

Potassium acetate may contain the same impurities as the sodium salt. The di- and tri-acetates are prepared like those of sodium.

Sodium acetate $C_2H_3O_2Na$ is formed (1) by the action of dilute acetic acid on sodium carbonate, the solution being evaporated and crystallised; (2) by neutralisation of pyroligneous acid with soda, and evaporation and fusion of the salt to remove tarry matters; (3) by the addition of Glauber's salt to solution of acetate of lime or of lead. The solution is decanted and filtered from the precipitated calcium or lead sulphate, evaporated and crystallised, and the crystals dissolved and recrystallised. Methods (2) and (3) are used on the manufacturing scale.

Sodium acetate forms monoclinic crystals, containing 3 molecules of water; has a strong saline taste; is soluble in 2·8 parts cold water and in 0·5 boiling water. The crystals melt completely at 75° and lose their water of crystallisation at 100°. By solution of this salt in ordinary strong acetic acid and rapid evaporation the diacetate of soda is formed; when glacial acid is used the triacetate is produced.

Sodium acetate is used for the preparation of acetic acid and in medicine; for the preservation of meat and other foods instead of salt. The saturated solution is occasionally used for filling carriage foot-warmers.

The commercial acetate is liable to contain sulphates, chlorides and carbonates, and metallic salts. Tarry matters are frequently present from the pyroligneous acid used in its manufacture. Acetate of lime, and sulphate and carbonate of potash are occasionally added as adulterants.

For the estimation of acetic acid in commercial acetates the method of Stillwell and Gladding in a modified form is used (*v. supra*).

Alkyl Acetates. *Acetic ethers.*

Acetic acid forms numerous acetates with organic radicles. Some of these occur in the oils from various seeds.

Amyl acetates $C_5H_{11}(C_2H_3O_2)$.

The following isomeric amyl acetates are known:—

1. Normal amyl acetate, boiling at 147·6° (Gartenmeister); at 148·4° (737 mm.) (Lieben and Rossi).

2. *Iso*amyl acetate.

3. Methyl propyl carbinyl acetate, boiling at 133°–135° (Wurtz); at 134°–137° (Schorlemmer).

4. Methyl *iso*propyl carbinyl acetate, boiling at 125° (Wurtz).

5. Diethyl carbinyl acetate, boiling at 132° (741 mm.) (Wagner and Saytzeff).

6. Tertiary amyl acetate, boiling at 124° (750 mm.) (Flavitzky).

Of these, only the second is of technical interest.

*iso*Amyl acetate, generally known as *amyl acetate* $(CH_3)_2CH{\cdot}CH_2CH_2O{\cdot}C_2H_3O$, is a colourless liquid of an odour resembling that of jargonelle pears. Sp.gr. 0·8762 15°/4° (Mendeléeff), 0·8562 22°/4° (Brühl), b.p. 138·5°–139° at 758·6 (Schiff).

It may be prepared by distilling a mixture of 1 part amyl alcohol, 1 part strong sulphuric acid, and 2 parts dried potassium acetate; or by warming a mixture of 1 part amyl alcohol, 1 part acetic acid and 0·5 part strong sulphuric acid on the water-bath and pouring the solution when cold into excess of water. The upper layer of purified amyl acetate is separated, shaken with a strong solution of sodium carbonate, again separated, dried over calcium chloride, and redistilled.

It may be prepared commercially from fusel oil, hydrochloric acid, and calcium acetate (Wilson, Eng. Pat. 4669). The commercial amyl acetate contains some of the other isomerides.

It is insoluble in water, but dissolves in all proportions in ether, amyl alcohol, and ordinary alcohol. The latter solution is largely used under the name of *Jargonelle pear essence* for flavouring confectionery.

Camphor, tannin, resins, &c., dissolve readily in amyl acetate. A solution of gun-cotton therein is used as a varnish, for lacquering metals, &c., and in the form of a stiff jelly, mixed with opaque substances such as china clay, as a substitute for celluloid.

It is also used in the manufacture of photographic films and in some smokeless powders.

It has been recommended for use for the production of a standard flame in photometry (J. Soc. Chem. Ind. 1885, 262).

The Hefner standard lamp burns amyl acetate as an illuminant.

Ethyl acetate. *Acetic ether* $C_2H_5(C_2H_3O_2)$ is a fragrant limpid liquid of sp.gr. 0·9072 15°/15°, b.p. 77·5° (Perkin); sp.gr. 0·92446 0°/4°, b.p. 77·17° at 760 mm. (Young and Forty).

For the preparation of acetic ether 3·6 pts. by weight of commercial absolute alcohol is mixed with 9 pts. sulphuric acid with constant stirring. After standing twenty-four hours the mixture is poured on 6 pts. of fused sodium acetate (in small lumps), allowed to stand for twelve hours and distilled. The product is rectified over calcium chloride and carbonate of potash and redistilled. Clark recommends the following process: 283 c.c. (10 oz.) of rectified alcohol (sp. gr. 0·838) are placed in a flask, and 283 c.c. of sulphuric acid (B.P.) are added with constant stirring. The liquid should be cooled externally as far as possible, allowed to stand till the temperature has sunk to 15°, and 351 grams (12¾ oz.) of dried sodium acetate added gradually with constant stirring and cooling. The liquid is distilled until 400 c.c. (14 oz.) has passed over; this is digested for three days with 2 oz. freshly dried potassium carbonate and filtered. The filtrate is distilled on the water-bath until all but 1 oz. has passed over. On the large scale dried sodium acetate may be substituted for the potassium carbonate with advantage (*v.* further W. I. Clark, Pharm. J. [3] 1883, 777).

Ethyl acetate is soluble in 8 parts of water at 0°, and somewhat *less* soluble in water at 15°. On the other hand, 1 part water dissolves

26 parts of the acetate at 0° and 24 parts at 15°.

Commercial acetic ether usually contains less than 75 p.c. of ethyl acetate, the rest being acetic acid, alcohol, water, ether, &c. It occurs, together with other organic acetates, in vinegar and wines.

Methyl acetate $CH_3(C_2H_3O_2)$ is a colourless fragrant liquid of sp.gr. 0·9398 15°/15°, boiling at 57·5° (760 mm.) (Perkin). It occurs in wood-spirit, and in crude wood-vinegar.

Methyl acetate is best prepared by distilling a mixture of 1 part methyl alcohol, 1 part potassium acetate, and 2 parts sulphuric acid. The product is dried over calcium chloride and quicklime and redistilled. It is soluble in water, alcohol, and ether.

ACETINS. The acetins are the acetyl derivatives of glycerol, or glycerol acetates. Five of these are theoretically possible, two mono-, two di-, and one tri- derivative, according to the number and position of the hydroxyl groups attacked by the acetic acid. Only three of these compounds have been prepared so far, one in each class, and the positions which the acetyl groups take up in the mono- and di- derivatives does not appear to be experimentally proved, though they are probably terminal. Commercial acetin is a mixture of all three compounds with other products.

The following method for the preparation of mono-, di-, and tri-acetin has been described by A. C. Geitel (J. pr. Chem. 1897, [ii.] 55, 417):—

200 grams of dry glycerol are heated with 500 grams of glacial acetic acid for 8 hours, and the acetic acid and water distilled off under reduced pressure. A further quantity of 150 grams acid is then added, and the heating continued for 16 hours. *Triacetin* is isolated from the product by diluting with water and extracting with ether, and is a colourless liquid, dissolving in water to the extent of about 7 p.c. at 15°. It has a sp.gr. 1·1605 at 15° and distils without decomposition at 172°–172·50/40 mm. *Diacetin* is obtained from the remaining solution by fractionating (after concentration) under a pressure of 40 mm., when it comes over between 175°–176°. It is a soluble colourless liquid with sp.gr. 1·1769 at 15°. In order to isolate the monoacetin formed in the reaction the aqueous solution after removal of the triacetin is extracted for 8 hours with ether at 34°–35° in an extracting apparatus for liquids; the later extracts are collected separately, diluted with an equal volume of water, and, after being extracted with hot benzene, are concentrated. The monacetin thus formed is a thick syrup of sp.gr. 1·2212 at 15°. By prolonging the ether extraction still further *monacetyldiglycerol* $C_3H_5(OH)_2{\cdot}O{\cdot}C_3H_5(OAc){\cdot}OH$ may be obtained; it is a colourless liquid of sp.gr. 1·2323 at 15°. *Diacetyldiglycide* may also be separated from the monacetin by fractionation, and *triacetyldiglycerol* is also formed.

Commercial Acetin (' *Acetine* ') is prepared by heating in an oil-bath a mixture of 60 parts of glycerol and 82 parts of glacial acetic acid for 12–15 hours at 120°, and gradually raising the temperature to 160° to expel the excess of acetic acid. The product is a thick liquid smelling of acetic acid and varying in colour from light yellow to dark brown, according to the purity of the glycerol used.

The value of the product depends upon the extent to which combination has taken place, and this is determined by observing the specific gravity and estimating the free and combined acetic acid. The density varies between 1·1608 and 1·1896, being lowest when the free acetic acid is present in largest amount. The free and combined acetic acid are determined as follows: 50 grams of 'acetin' are diluted with water to 500 c.c. The free acid in 50 c.c. of this solution is determined by titration with normal caustic soda, using phenolphthalein as indicator. 15 c.c. of normal caustic soda are added to 10 c.c. of the acetin solution, and the combined acetic acid liberated by hydrolysis by boiling for five minutes. The excess of caustic soda remaining is a measure of the total acid present; and the amount of combined acid is found by subtracting from the amount of caustic soda used up in the hydrolysis the quantity accounted for by the free acid. The following table (Kopp and Grandmougin, Bull. Soc. Ind. Mulhouse, 1894, 112) shows the results of typical analyses:—

No.	Density	Acid free	Acid combined	Remarks
		p.c.	p.c.	
1	1·1774	9·2	46·0	A medium quality sample
2	1·1896	6·98	55·7	A good sample
3	1·1608	23·0	43·5	Poor sample.

Acetin is used as a solvent for basic colouring matters, such as Induline and Perkin's violet. They are dissolved by being heated together for about two hours, cooling, and filtering through a silk filter. Acetin is to be preferred to ethyl and methyl tartaric acids as a solvent, as acetic acid is less injurious to the fibres than tartaric acid.

Halogen derivatives of the Acetins.

$\alpha\gamma$-dibromo-β-acetylglycerol $(CH_2Br)_2CH{\cdot}OAc$ is obtained by the prolonged action of hydrogen bromide on triacetin, or by heating the mixture to 100° in sealed tubes; it boils at 130°–135° (40 mm.) and has sp.gr. 1·5880 at 15°. It has an agreeable aromatic odour, is slightly soluble in water, and readily soluble in alcohol and ether. It yields *iso*propyl alcohol on reduction.

α-bromo-$\beta\gamma$-diacetylglycerol $CH_2Br{\cdot}CH(OAc){\cdot}CH_2{\cdot}OAc$ is produced by the prolonged action of hydrogen bromide dissolved in acetic acid on triacetin at 0° in the dark. It boils at 150°–155° (40 mm.), and has sp.gr. 1·2905 at 15°. It yields *iso*propylene glycol on reduction.

$\alpha\gamma$-dichloro-β-acetylglycerol $(CH_2Cl)_2CH{\cdot}OAc$ prepared similarly to the bromine compound, boils at 115°–120° (40 mm.), and has sp.gr. 1·1618 at 15°.

α-chloro-$\beta\gamma$-diacetylglycerol $CH_2Cl{\cdot}CH(OAc)CH_2{\cdot}OAc$ boils at 145°–150° (40 mm.), and has sp.gr. 1·1307 at 15°.

$\alpha\beta$-dichloromonoacetin $CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OAc$ is prepared by the action of acetic anhydride on chlorinated allyl alcohol, and has sp.gr. 1·1677 at 15°, but in all other respects is identical with the $\alpha\gamma$-dichloro- compound.

α-iododiacetin $CH_2I{\cdot}CH(OAc){\cdot}CH_2{\cdot}OAc$ is

obtained by the action of sodium iodide on the corresponding chloro- compound. It is an unstable oil having a sp.gr. 1.4584 at 15°.

J. A. P.

ACETOACETIC ACID $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ is a thick acid liquid miscible with water in all proportions. It is prepared from its ethyl ester by leaving 4½ parts of ester in contact with 2·1 parts of potash and 80 parts of water for 24 hours and acidifying with sulphuric acid. It is extracted from the solution with ether.

It is very unstable and readily decomposes below 100° into acetone and carbon dioxide. It yields a violet colouration with ferric chloride and forms ill-characterised amorphous salts, $BaA_2,2H_2O$ and $CuA_2,2H_2O$, when treated with the corresponding carbonate.

Acetoacetic acid appears in the urine of diabetic patients, and indicates defective oxidation. Its detection and estimation have been the subject of much controversy and investigation. Arnold (Chem. Zentr. 1899, ii. 146) makes use of a colour reaction with acetophenone, which will show 1 part in 10,000, but is affected to some extent by the presence of acetone. Riegler (Chem. Soc. Abstr. 1903, ii. 112) employs the colour produced by the addition of sulphuric and iodic acids, which he states to be unaffected by the presence of sugars, leucine, tyrosine, or acetone. Bondi (Chem. Zentr. 1906, i. 707) recommends the use of a solution of iodine and the detection of acetoacetic acid by the characteristic smell of the iodacetone produced; but Lindemann (*ibid.* 717) says that this smell is not characteristic of acetoacetic acid. Mayer adds the urine to a very dilute solution of ferric chloride in brine, when, in the presence of acetoacetic acid, a claret-red ring is formed. When the red colour is only just visible, the liquid may be assumed to contain 0·01 p.c. of the acid. A blank test performed after boiling the acid for five minutes should give no colour (Chem. Zentr. 1906, i. 406).

Messinger's process as modified by Huppert (Analyse des Harns, 1898) estimates the total amount of acetone and acetoacetic acid present with fair accuracy, and the acetone may be estimated separately with considerable exactitude by the method of Folin (J. Biol. Chem. 1907, 3, 177), in which it is aspirated out of the liquid into iodine and potash, and the resulting iodoform weighed.

Methyl acetoacetate $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$ is prepared by heating together methyl acetate and sodium under a reflux condenser and subsequently distilling in a stream of carbon dioxide. It is a colourless liquid, easily miscible with water, which boils at 169°–170° and has a sp.gr. 1·0917 at 4°; 1·0809 at 15°; and 1·0724 at 25°. It is decomposed on boiling with water into carbon dioxide, acetone, and methyl alcohol. With ferric chloride it yields a deep red colouration.

Ethyl acetoacetate (*acetoacetic ether*) $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ and $CH_3{\cdot}C(OH):CH{\cdot}CO_2Et$, was discovered by Geuther in 1863, and independently by Frankland and Duppa in 1865. It is a colourless, slightly syrupy liquid, with a pleasant odour. It boils at 180·6°–181·2°/754 mm. (Brühl); 180°–180·3° /754·5 mm. (Schiff); 71°/12·5 mm. and 100·2°/80mm. (Kahlbaum). It has a specific gravity 1·0465 0°/4° (Schiff); 1·0282 20°/4° (Schaum).

Ethyl acetoacetate is prepared by the action of sodium on ethyl acetate. The following details of the method are given by Conrad (Annalen, 186, 214): 100 grams of sodium are added to 1000 grams of pure ethyl acetate, and after the reaction has moderated considerably, the whole is heated on a water-bath under a reflux condenser for 2–2½ hours until all the sodium has disappeared. To the warm mass 550 grams of 50 p.c. acetic acid are added, and after cooling 500 c.c. of water. The whole is well shaken, and the upper layer separated, washed with a little water, and fractionated. The fractions 100°–130°, 130°–165°, 165°–175°, 175°–185°, 185°–200° are collected separately and refractionated twice. The yield is 175 grams of product boiling at 175°–185°, and from the fraction boiling below 100°, 350–400 grams of ethyl acetate may be recovered after removing the alcohol by salting out.

Ethyl acetoacetate is neutral to litmus, but forms salts with sodium, copper, and other metals by replacement of hydrogen. Only one atom of hydrogen can be replaced by sodium, but if the sodium in the resulting compound is replaced by an alkyl radicle a second hydrogen atom may then be replaced. Ferric chloride produces a violet colouration. With sodium bisulphite a crystalline addition product $C_6H_{10}O_3$, $NaHSO_3$ is formed. On heating for a long time, or leading the vapour through a hot tube, acetone, alcohol, dehydracetic acid, and methane are formed. Sodium amalgam reduces it to *β-hydroxy butyric* acid $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$. It condenses with hydroxylamine, but does not form an oxime, as internal condensation takes place, resulting in the production of *methyl isoxazolone* $CH_3{\cdot}C{<}\begin{matrix}\cdot\\ N\text{——}O\end{matrix}{>}CH_2{\cdot}CO$ which is converted by alkalis into salts of *β*-oximinobutyric acid.

Applications in Synthesis.—By means of ethyl acetoacetate fatty acids, ketones, and many ring compounds may be prepared.

Fatty acids may be obtained by dissolving sodium (1 atom) in absolute alcohol, adding ethyl acetoacetate (1 mol.) followed by an alkyl halogen compound (1 mol.). The resulting alkyl derivative is treated with strong alkalis, when the molecule is hydrolysed with formation of acetic acid and the desired alkyl acetic acid.

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H \rightarrow CH_3{\cdot}C(ONa):CH{\cdot}CO_2Et \rightarrow CH_3{\cdot}CO{\cdot}CHR{\cdot}CO_2Et \rightarrow CH_3{\cdot}CO_2H + RCH_2{\cdot}CO_2H.$$

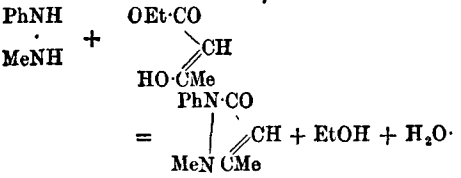
If the hydrolysis is brought about by *dilute acids* instead of concentrated alkalis, the molecule is differently divided, producing ketones.

$$CH_3{\cdot}CO{\cdot}CHR{\cdot}CO_2Et \rightarrow CH_3CO{\cdot}CH_2R + EtOH + CO_2.$$

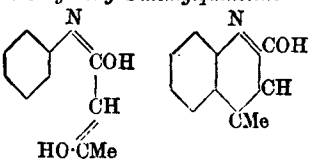
Dialkyl acetic acids and ketones may be produced by introducing a second alkyl radicle into the molecule by a similar process after the first has entered, but the two cannot be introduced together in one operation.

Pyrazolones, of which the most important industrially is *antipyrine*, are produced by the condensation of ethyl acetoacetate with hydrazines. Antipyrin (*1-phenyl 2:3-dimethyl-5-pyrazolone*) is prepared from symmetrical methyl

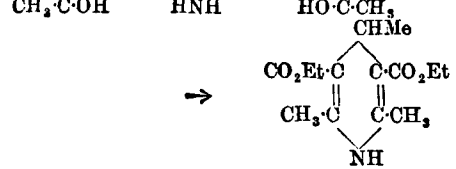
phenylhydrazine and ethyl acetoacetate (*v.* also PYRAZOLE and ANTIPYRINE).



Quinolines may be prepared by first making the anilide of ethyl acetoacetate by heating with aniline at 110°, and afterwards heating this product with concentrated hydrochloric acid. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ changes into $CH_3{\cdot}C(OH):CH{\cdot}C(OH):NPh$, and readily condenses to *1-hydroxy-4-methylquinoline*



Pyridines (*v.* also BONE OIL) are obtained by condensing ethyl acetoacetate with aldehyde ammonias. Ethyl dihydrocollidine dicarboxylate is the simplest example:



Pyrones.—Dehydracetic acid, α-methyl β-acetylpyrone, is produced on heating ethyl acetoacetate for a considerable time.

Constitution.—The constitution of ethyl acetoacetate and its sodium derivatives was for many years a subject of discussion by Frankland and Duppa, Geuther, Claisen, Laar, Wislicenus, Brühl, Perkin, and others. The general opinion is that ethyl acetoacetate consists of a mixture of the two forms, ketonic $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, and enolic $CH_3{\cdot}C(OH):CH{\cdot}CO_2Et$. The freshly prepared substance is practically a pure ketone, but on keeping it changes partially into the enolic form, and when equilibrium is reached about 10 p.c. of the latter is present at ordinary temperatures. The sodium compound is a derivative of the enolic form.

Alkyl derivatives of ethyl acetoacetate.

1. *Mono-substituted alkyl derivatives.*

Ethyl methylacetoacetate $CH_3{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$ boils at 186·8°, and has sp.gr. 1·009 at 6°. Prepared from methyl iodide and sodium acetoacetate (Geuther, J. 1865, 303).

Ethyl ethylacetoacetate $CH_3{\cdot}CO{\cdot}CHEt{\cdot}CO_2Et$ boils at 195°–196°, and has sp.gr. 0·9834 at 16°. It is readily decomposed by baryta or alcoholic potash into alcohol, carbon dioxide and methyl propyl ketone; and by dry sodium ethoxide into acetic and butyric esters (Miller, Annalen, 200, 281; Wedel, Annalen, 210, 100; Frankland and Duppa, Annalen, 138, 215; Wislicenus, Annalen, 186, 187).

Ethyl propylacetoacetate $CH_3{\cdot}CO{\cdot}CHPr^{\alpha}{\cdot}CO_2Et$ boils at 208°–209°, and has sp.gr. 0·981 at 0°/4°. It is prepared by adding to a solution of 27 grams of sodium in 270 grams absolute alcohol, 152·7 grams ethyl acetoacetate, followed gradually by 206 grams propyl iodide.

Ethyl isopropylacetoacetate $CH_3{\cdot}CO{\cdot}CHPr^{\beta}{\cdot}CO_2Et$ boils at 201°/758·4, and has sp.gr. 0·9805 at 0°.

Ethyl isobutylacetoacetate $CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CHMe_2){\cdot}CO_2Et$ boils at 217°–218°, and has sp.gr. 0·951 at 17·5° (Rohn, Annalen, 190, 306; Minter, Ber. 1874, 501).

Ethyl isoamylacetoacetate $CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CHMe_2)CO_2Et$ boils at 227°–228° (Peters, Ber. 1887, 3322).

Ethyl amylacetoacetate $CH_3{\cdot}CO{\cdot}CH(C_5H_{11})CO_2Et$ boils at 242°–244° (Ponzio and Prandi, Gazz. chem. ital. 28, ii. 280).

Ethyl heptylacetoacetate boils at 271°–273°, and has sp.gr. 0·9324 at 17·7°.

Ethyl octylacetoacetate boils at 280°–282°, and has sp.gr. 0·9354 at 18°·5/17·5°.

2. *Di-substituted alkyl derivatives.*

Ethyl dimethylacetoacetate $CH_3{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$ boils at 184°, and has sp.gr. 0·9913 at 16°.

Ethyl methylethylacetoacetate $CH_3{\cdot}CO{\cdot}CMeEt{\cdot}CO_2Et$ boils at 198°, and has sp.gr. 0·947 at 22°/17°·5.

Ethyl methylpropylacetoacetate $CH_3{\cdot}CO{\cdot}CMePrCO_2Et$ boils at 214°, and has sp.gr. 0·9575 at 17°/4°.

Ethyl diethylacetoacetate $CH_3{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et$ boils at 218°, and has sp.gr. 0·9738 at 20°.

Ethyl dipropylacetoacetate $CH_3{\cdot}CO{\cdot}CPr_2{\cdot}CO_2Et$ boils at 236°, and has sp.gr. 0·9585 at 0°/4°.

Ethyl diisobutylacetoacetate boils at 250°–253°, and has sp.gr. 0·947 at 10°.

Ethyl diheptylacetoacetate boils at 332°, and has sp.gr. 0·891 at 17·5°/17·5°.

Ethyl dioctylacetoacetate boils at 264°/90 mm., 340°–342°/760 mm.

ACETOL. Obtained as an ester of salicylic acid by condensing sodium salicylate with monochloracetone $OH{\cdot}C_6H_4{\cdot}COO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$. Forms needles from solution in alcohol, m.p. 71°; sparingly soluble in warm water (Fritsch, E. P. 3961, 1893; J. Soc. Chem. Ind. 1894, 274).

ACETOMETER. A hydrometer graduated to indicate the strength of commercial acetic acid according to its density.

ACETONE C_3H_6O or $CH_3{\cdot}CO{\cdot}CH_3$. *Dimethyl ketone.* A product of the destructive distillation of acetates; obtained by Liebig from lead acetate (Annalen, I, 225) and further examined by Dumas (Ann. Chim. Phys. [2] 49, 208), who first determined its composition. Acetone is also produced in the dry distillation of wood (Völckel, Annalen, 80, 310; J. Soc. Chem. Ind. 16, 667, 722; 27, 798); of citric acid (Robiquet, B. J. 18, 502); of sugar, starch, and gums with lime (Frémy, Annalen, 15, 279; J. Soc. Chem. Ind. 21, 541, 1096). By oxidation of proteid substances with iron salts (Blumenthal and Neuberg, Chem. Zentr. 1901, i. 788; Ingler, Beitr. Chem. Phys. Path. 1902, i. 583), and by heating citric acid with potassium permanganate (Péan de St. Gilles, J. 1858, 585; Sabbatani, Atti Acad. Sci. Torino, 1900, 35, 678); and by the oxidation of *iso*valeric acid (Crossley and Le Sueur, Chem. Soc. Trans. 1899, 165).

Preparation.—1. Acetone can be obtained by distilling a mixture of 1 part of caustic lime and 2 parts of crystallised lead acetate (Zeise, Annalen, 33, 32); but is usually prepared by the dry distillation of barium acetate at a moderate heat. Calcium acetate can also be employed, but the temperature required is greater, and the product is contaminated with impurities, such as *dumasin*, an isomeride of mesityl oxide; but according to Becker (J. Soc. Chem. Ind. 26, 279) a lower temperature is required if the calcium salts are made quite neutral and the formation of free lime is prevented by the introduction of a stream of dry carbon dioxide. Magnesium or strontium acetates can also be used. Industrially, acetone can be prepared by passing the vapour of acetic acid into air-tight vessels heated to 500°, containing some porous substances saturated with lime or baryta (J. Soc. Chem. Ind. 18, 128, 824; Bauschlicker, D. R. P. 81914); also by passing a continuous current of pyroligneous acid over a heated acetate capable of forming acetone (J. Soc. Chem. Ind. 25, 634; 26, 1002; 27, 277). An improved method is also described by Wenghöffer (D. R. P. 144328; compare also J. Soc. Chem. Ind. 14, 987; 20, 1130; 22, 297).

According to Squibb (J. Soc. Chem. Ind. 1896, 231; J. Amer. Chem. Soc.), pure acetone for use in the preparation of smokeless powders can be obtained by subjecting acetates mixed with an excess of calcium hydroxide to destructive distillation and to the action of superheated steam.

2. From wood-spirit acetone can be separated by distilling over calcium chloride. The product obtained by these methods can readily be purified by converting the acetone into its crystalline compound with acid sodium (or potassium) sulphite, crystallising this, and subsequently distilling with aqueous sodium carbonate; the distillate is then treated with concentrated calcium chloride solution and the ethereal layer rectified over solid chloride. According to Conroy (J. Soc. Chem. Ind. 19, 206), it should be purified by distillation over sulphuric acid (Dott, J. Soc. Chem. Ind. 27, 272), whilst Arnoult (*ibid.* 27, 679) recommends treatment with oxidising agents.

Acetone has been prepared synthetically from zinc methyl and acetyl chloride (Freund, Annalen, 118, 11). It occurs in the urine, blood, and brain of calcium diabetic patients.

Properties.—Acetone is a limpid, mobile liquid, having an agreeable odour and a peppermint-like taste. It is very inflammable and burns with a white smokeless flame, b.p. 56·3° (Regnault); sp.gr. 0·8144 at 0°, 0·79945 at 13·9° (Kopp, Annalen, 64, 214); b.p. 56·53° (corr.) and sp.gr. 0·81858 at 0°/4° (Thorpe, Chem. Soc. Trans. 37, 212); sp.gr. 0·81378 at 0°/4°, 0·79705 at 15°/4°, 0·77986 at 30°/°4 (Saposchnikoff, J. Russ. Phys. Chem. Soc. 28, 229); m.p.—94·9° (Ladenburg and Krügel, Ber. 32, 1821; Formenti, L'Orosi, 1900, 23, 223). Acetone is miscible in all proportions with water, alcohol, ether, and many ethereal salts; it can be separated from its aqueous solution by the addition of calcium chloride, and dissolves many fats and resins. It is also an excellent solvent for acetylene and tannins (Trimble and Peacock, Pharm. J. 53, 317). Acetone is used in perfumery and pharmacy; in the manufacture of smokeless powders; of cordite and of celluloid articles (Marshal, J. Soc. Chem. Ind. 23, 24, 645), also in the preparation of iodoform (Teeple, J. Amer. Chem. Soc. 26, 170; Abbott, J. Phys. Chem. 7, 83); of chloroform (Squibb, J. Amer. Chem. Soc. 1896, 231; Orndorff and Jessel, Amer. Chem. J. 10, 363; Dolt, *l.c.* 271); and in the presence of sodium sulphite it can be used as a good substitute for alkali in photographic developers (Lumière and Segewetz, Bull. Soc. chim. 15, [3] 1164; Mon. Sci. 1903, 257, 568; Eichengrün, Zeitsch. angew. Chem. 1902, 1114). When its vapour is passed through a red-hot copper tube, a very small proportion of tarry products containing naphthalene is obtained together with a large volume of gas having the composition: carbon monoxide, 39·23 p.c.; methane, 37·58 p.c.; hydrogen, 17·54 p.c.; and ethylene, 5·65 p.c. (Barbier and Roux, Compt. rend. 102, 1559). Dehydrating agents readily act on acetone and convert it into condensation products; thus, caustic lime converts acetone into mesityl oxide $C_6H_{10}O$ and phorone $C_9H_{14}O$ when the action is allowed to continue for a week (Fittig, Annalen, 110, 32), and, together with smaller proportions of other products, these two compounds are also formed when it is saturated with hydrogen chloride and allowed to stand for 8 to 14 days (Baeyer, Annalen, 140, 297): with zinc chloride terpene condensation products are formed (Raikow, Ber. 30, 905). Distillation with concentrated sulphuric acid converts acetone into mesitylene, mesityl oxide, phorone and *iso*durene and other substances (Orndorff and Young, Amer. Chem. J. 15, 249). A similar result is obtained when it is heated with boron fluoride. The action of nitric acid and nitric oxide on acetone has been studied by Newbury and Orndoff (Amer. Chem. J. 12, 517), Behrend and Schmitz (Annalen, 277, 310), Behrend and Tryller (Annalen, 283, 209), Apetz and Hell (Ber. 27, 933), Traube (Annalen, 300, 81), McIntosh (Amer. Chem. Soc. 27, 1013); of hydrogen peroxide by Baeyer and Villiger (Ber. 32, 3625; 33, 174, 858), Pastureau (Compt. rend. 140, 1591), Wolffenstein (Ber. 28, 2265); of thionyl chloride by Loth and Michaels (Ber. 27, 2540); and of hypophosphorous acid by Marie (Compt. rend. 133, 219).

Sodium in the presence of water reduces acetone to *iso*propyl alcohol and pinacone (Fittig, Annalen, 110, 25; 114, 54; Städeler, Annalen, 111, 277; Friedel, Annalen, 124, 329), but when the materials are quite dry and air is excluded, sodium acetonate is formed (Freer, Amer. Chem. J. 12, 355; 13, 308; 15, 582; Taylor, Chem. Soc. Trans. 1906, 1258; Bacon and Freer, Philippine J. Sci. 1907, 2, 67). Red-hot magnesium acts on acetone, yielding hydrogen and allylene, whilst magnesium amalgam forms magnesium acetonate which is rapidly decomposed by water, yielding pinacone hydrate (Keiser, Amer. Chem. J. 18, 328; Conturier and Meunier, Compt. rend. 140, 721). Chlorine, bromine, and iodine in the presence of alkalis convert acetone into chloroform, bromoform, and iodoform respectively.

Reactions.—When quite pure acetone should remain perfectly colourless on exposure to light, and should not be attacked by potassium

permanganate in the cold; in the presence of alkali, however, and on warming, carbonic and oxalic acids are formed (Cochenhausen, J. pr. Chem. 166, 451; Conroy, J. Soc. Chem. Ind. 19, 206; Fournier, Bull. Soc. chim. 1908, 3, 259). Acetone, when treated with aqueous potash and iodine, yields iodoform (Lieben). Gunning (Zeitsch. anal. Chem. 24, 147) has modified this reaction to render it available when alcohol is present by employing ammonia and a solution of iodine in ammonium iodide. Another test proposed by Reynolds (*ibid.* 24, 147) is based on the fact that mercuric oxide is soluble in acetone in the presence of potassium hydroxide; the suspected liquid is mixed with a solution of mercuric chloride rendered strongly alkaline with alcoholic potash, and after shaking the mixture is filtered and the filtrate tested for mercury by means of ammonium sulphide or stannous chloride. Denigès (Compt. rend. 126, 1868; 127, 963; Bull. Soc. chim. 13, [3] 543; 19, [3] 754) recommends the use of the additive compound formed by acetone with mercury sulphate, for detecting acetone in methyl and ethyl alcohol (Oppenheimer, Ber. 32, 986). Penzoldt (Zeitsch. anal. Chem. 24, 147) adds to the suspected liquid orthonitrobenzaldehyde, which in presence of caustic alkali combines with acetone to form indigo. Another delicate test is to add sodium hydroxide, hydroxylamine and pyridine, then ether and bromine until the solution is yellow, hydrogen peroxide is now added when, if acetone is present, the solution becomes blue (Stock); dimethyl *p*-phenylenediamine produces a red colouration which changes to violet on addition of alkali or acid (Malerba, Zeitsch. anal. Chem. 37, 690). Similar colour reactions are obtained by adding a few drops of sodium nitroprusside to a mixture of acetone and a primary aliphatic amine (Rimini, Chem. Zentr. 1898, 2, 132). Of all these tests Lieben's is perhaps the most sensitive. To detect acetone in urine a strong solution of sodium nitroprusside is added, then the mixture made alkaline with potash, when a red colouration is produced which changes to violet on addition of acetic acid (Legal, J. Pharm. Chim. 1888, 17, 206; Denigès, Bull. Soc. chim. [3] 15, 1058). According to Egeling (Chem. Zentr. 1894, ii. 457), it is best to use ammonia, when a brilliant violet colour is at once produced: this reaction is not given by aldehyde. For other methods of detecting and estimating acetone, compare Arachequesne, Compt. rend. 110, 642; Collischonn, Zeitsch. anal. Chem. 29, 562; Squibb, J. Amer. Chem. Soc. 18, 1068; Kebler, *ibid.* 19, 316; Schwicker, Chem. Zeit. 15, 914; Strache, Monatsh. 13, 299; Klar, J. Soc. Chem. Ind. 15, 299; Hintz, Zeitsch. anal. Chem. 27, 182; Sternberg, Chem. Zentr. 1901, i. 270; Keppeler, Zeitsch. angew. Chem. 18, 464; Vaubel and Schleuer, *ibid.* 18, 214; Jolles, Ber. 39, 1306; Auld, J. Soc. Chem. Ind. 25, 100; Heikel, Chem. Zeit. 32, 75.

(For estimating acetone in wood spirit, *see* Arachequesne, *l.c.*; Vignon, Compt. rend. 110, 534; 112, 873; and in urine, *see* Huppert, Zeitsch. anal. Chem. 29, 632; Salkowski, J. Pharm. Chim. 1891, 194; Geelmuyden, Zeitsch. anal. Chem. 35, 503; Willen, Chem. Zentr. 1897, i. 134; Martz, ii. 232; Argenson, Bull. Soc. chim. 15, [3] 1055; Studer, Chem. Zentr. 1898, i. 1152; Mallat, J. Pharm. 1897, 6296; Sabbatani, Chem. Zentr. 1899, ii. 22; Riegler, Zeitsch. anal. Chem. 40, 94; Vournasos, Bull. Soc. chim. 31, [3] 137; Graaff, Pharm. Weekblad, 1907, 44, 555; Folin, J. Biol. Chem. 1907, 3, 177; Monimart, J. Pharm. Chem. 1892, 26, 392; Heikel, *l.c.*; Hart, J. Biol. Chem. 1908, 4, 477.)

Derivatives.—Acetone combines directly with a large number of substances yielding well-characterised additive compounds. 1. *Compounds with alkaline sulphites*:—Acetone forms definite crystalline compounds when shaken with concentrated solutions of the acid sulphites (bisulphites) of the alkali metals (Precht, Phot. Centr. 1902, 8, 301; Kerp, Kaiserl. Gesundh. 1904, 21, 40; Rothwood, Monatsh. 26, 1545). The *potassium* salt $C_3H_6O,KHSO_3$, and the *sodium* salt $C_3H_6O,NaHSO_3$, crystallise in nacreous scales (Limpricht, Annalen 93, 238); the *ammonium* salt C_3H_6O,NH_4HSO_3 crystallises in laminæ (Städeler, Annalen, 111, 307). The *barium* salt has formula $2C_3H_6O,Ba(SO_3H)_2,H_2O$ (Fagard, J. Pharm. Chim. 1895, 2, 145). These salts yield acetone when heated with aqueous potash. —2. *Compounds with chloroform* (Willgerodt, Ber. 14, 2451; 15, 2308; Cameron and Holly, Chem. Zentr. 1898, ii. 277; Jocitsch, *ibid.* 1899, i. 606; Willgerodt and Dürr, J. pr. Chem. 148, 283). —3. *Compounds with hydrogen cyanide* (Urech, Annalen, 164, 255):—Acetone yields acetonecyanhydrol C_4H_7NO, b.p. 120°, when added to anhydrous hydrogen cyanide; and diacetonecyanhydrol $C_7H_{13}NO_2$, a crystalline substance, when treated with a 25 p.c. solution (aqueous) of hydrogen cyanide (Tiemann and Friedländer, Ber. 14, 1965); with 3·3 p.c. hydrogen cyanide acetonecyanhydrin is obtained in the dark, but in the light a mixture of products is formed (Silber, Ber. 38, 1671).—4. *Compounds with ammonia*:—Ammonia unites with acetone in the cold with the elimination of the elements of water; the reaction, however, proceeds more quickly if the temperature is raised to 100°, or if dry ammonia gas is passed into boiling acetone. Several bases, diacetonamine $C_6H_{13}NO$, triacetonamine $C_9H_{17}NO$, triacetonediamine $C_9H_{20}N_2O$, and dehydrotriacetonamine $C_9H_{15}N$; the last two in very small quantity only, have been obtained by these methods, the relative proportions in which they are formed varying with the temperature and time employed. These bases and their derivatives have been examined by Heintz (Annalen, 174, 133; 175, 252; 178, 305, 326; 181, 70; 183, 276; 189, 214; 191, 122; 198, 42, 87; 201, 90; 203, 336) and by Sokolow and Latschinow (Ber. 7, 1384), Ruhemann and Carnegie (Chem. Soc. Trans. 1888, 424), Rügheimer (Ber. 21, 3325; 25, 1562), Harries (Annalen, 296, 328), Franchimont and Friedmann (Rec. Trav. Chim. 1907, 223), Gabriel and Colman (Ber. 35, 3805), Kohn and Lindauer (Monatsh. 23, 754), Kohn (Annalen, 351, 134; Monatsh. 24, 765, 773; 25, 135, 817, 850; 28, 429, 508, 529, 537, 1040); they yield well-crystallised salts, and can be separated from one another by means of their oxalates. Methylamine also gives corresponding compounds with acetone, but dimethylamine yields dimethyldiacetonamine as the sole product (Göttschmann, Annalen, 197, 27).

Thioacetones have been studied by Baumann and Fromm (Ber. 22, 1035, 2592).

Acetone forms compounds with mercuric sulphate (Denigès, *l.c.*; Oppenheimer, *l.c.*), with mercuric oxide (Auld and Hantzsch, Ber. 38, 2677; Lasserre, J. Pharm. Chim. 1890, 22, 246), with mercuric cyanide (Marsh and Struthers, Chem. Soc. Trans. 1905, 1878), with mercuric iodide (Gernez, Compt. rend. 137, 255; Marsh and Struthers, Chem. Soc. Proc. 1908, 266), and with mercuric nitrate (Hofmann, Ber. 31, 2212). Metallic derivatives of the type $CH_3{\cdot}CO{\cdot}CH_2K$ are obtained by the electrolysis of acetone solutions of potassium or sodium iodides or of potassium thiocyanate (Levi and Voghera, Gazz. chim. ital. 35, i. 277).

Acetone yields substitution derivatives when acted upon with chlorine or bromine (Bischoff, Ber. 5, 863, 963; 8, 1329). The following derivatives have been obtained:—Monochloracetone (Henry, Ber. 5, 190; Mulder, Ber. 5, 1009; Barbaglia, Ber. 7, 467; Linnemann, Annalen, 134, 171; Koenigs and Wagstaffe, Ber. 26, 554; Wislicenus, Kircheisen and Sattler, *ibid.* 26, 908; Fritsch, *ibid.* 26, 597; Tcherniac, Ber. 25, 2629; Kling, Bull. Soc. chim. [3] 33, 322); unsymmetrical dichloracetone (Fittig, Annalen, 110, 40; Borsche and Fittig, Annalen, 133, 112; Erlenbach, Annalen, 269, 46; Tcherniac, *l.c.*; Fritsch, *l.c.*; McIntosh, Chem. Soc. Trans. 1905, 790); symmetrical dichloracetone (Barbaglia, *l.c.*; Fritsch, *l.c.*); trichloracetone (Bischoff, *l.c.*; Kraemer, Ber. 7, 252; Perrier and Prost, Compt. rend. 140, 146; Hantzsch, Ber. 21, 242); tetrachloracetone (Bischoff, Levy, Witte and Curchod, Annalen, 252, 330, 254, 83; Levy and Jedlicka, Ber. 21, 318); and pentachloracetone (Cloëz, Bull. Soc. chim. [2] 39, 638; Fritsch, Annalen, 279, 310 and *l.c.*; Levy and Jedlicka, *l.c.*). The corresponding bromo-derivatives, with the exception of tribromacetone, are obtained by the direct action of bromine upon acetone (Mulder, J. 1864, 330; McIntosh, *l.c.*; Lapworth, Chem. Soc. Trans. 1904, 33), also by other methods (Hjelt and Siven, Ber. 21, 3288; Norton and Wistenhoff, Amer. Chem. J. 10, 213; Hantzsch, *l.c.*). Other halogen derivatives (J. Soc. Chem. Ind. 16, 933; Hantzsch, *l.c.* and Ber. 22, 1238) and the compounds of acetone with the halogen acids (Archibald and McIntosh, Chem. Soc. Trans. 1904, 924) have been described.

Acetone forms a large number of condensation products and derivatives with other organic compounds: Cyanacetones (Hantzsch, Ber. 23, 1472; Tcherniac, Ber. 25, 2607, 2621; Kowppa, Ber. 33, 3530). Acetone dioxalic ester obtained by the action of sodium ethylate on a mixture of acetone and oxalic ester is converted when treated with sodium ethoxide to a dienolic substance forming lemon-yellow needles, m.p. 98°, and dyeing wool in alcoholic solution. It is the first nitrogen free dye-stuff of the fatty series yet obtained (Willstatter and Pummerer, Ber. 37, 3733). Pseudo*cyclo*citralidene acetone and its homologues have an odour of violets, and are suitable for use in perfumes (J. Soc. Chem. Ind. 24, 290).

For acetone dicarboxylic acid and its derivatives, *see* Ormerod, Chem. Soc. Proc. 1906, 205; Denigès, Compt. rend. 128, 680; Lippmann, Ber. 41, 3981; for acetonyl acetone and its derivatives, *see* Knorr, Ber. 22, 168, 2100; Claisen and Ehrhardt, Ber. 22, 1009; Zincke and Kegel, Ber. 23, 230; Claisen, Ber. 25, 3164; the azo- (Bulow and Schlotterbeck, Ber. 35, 2187) and diazo- derivatives of acetonyl acetone, have dyeing properties (Faurel, Compt. rend. 128, 318).

Acetone, with diazobenzene chloride in the presence of alkali, yields a compound $C_{15}H_{14}ON_2$, m.p. 134°–135°, which has dyeing properties (Bamberger and Wulz, Ber. 24, 2793). For other condensation products compare Boessneck, Ber. 21, 1906; Pechmann and Wehsarg, *ibid.* 2989, 2994; Franke and Kohn, Monatsh. 19, 354; 20, 876; Spier, Ber. 28, 2531; Perkin and Thorpe, Chem. Soc. Trans. 1896, 1482; Weidel, Monatsh. 17, 401; Micko, *ibid.* 442; Stobbe Ber. 28, 1122; Cornelson and Kostanecki, Ber. 29, 240; Claisen, *ibid.* 2931; Röhmer, Ber. 31, 281; Pfitzinger, J. pr. Chem. 164, 283; Freer, Amer. Chem. J. 17, 1; Barbier and Bouveault, Compt. rend. 118, 198; Haller and March, Compt. rend. 139, 99; Straus, Ber. 37, 3293; Harries and Ferrari, Ber. 36, 656; Ulpiani and Bernardini, Atti R. Accad. Lincei, 1904, 13, 331; Pechmann and Sidgwick, Ber. 37, 3816; Duntwitz, Monatsh. 27, 773; Knoevenagel, Ber. 39, 3451, 3457; Purdie, Chem. Soc. Trans. 1906, 1200; Richard, Compt. rend. 145, 129. Diacetones and their derivatives have been studied by Combes (Compt. rend. 108, 1252; Behal and Auger, Compt. rend. 109, 970; Claisen and Stylos, Ber. 21, 141); derivatives of triacetone by Weinschenk (Ber. 34, 2185).

ACETONECHLOROFORM, *aaa-trichlor-β-hydroxy-β-methylpropane* (*Chloretone*) $(CH_3)_2{\cdot}C(OH){\cdot}CCl_3$, prepared by slowly adding powdered potassium hydroxide (3 parts) to a cooled mixture of acetone (5 parts) and chloroform (1 part) (Willgerodt, J. pr. Chem. [2] 37, 361) is a white crystalline compound, b.p. 167°, melting near but above 97°; it has a camphor-like odour, is soluble in hot, sparingly soluble in cold water, and crystallises well from ether, alcohol, acetic acid, acetone, or chloroform; it forms no definite hydrate, but the system acetone-chloroform/water presents a quadruple point for the solid, two solutions and the vapour at 75·2° (Cameron and Holly, J. Phys. Chem. 1898, 2, 322). The *acetate* $(CH_3)_2{\cdot}C(OAc){\cdot}CCl_3$ boils at 191°. The *benzoate* $(CH_3)_2{\cdot}C(OBz).CCl_3$ boils at 282° (Willgerodt and Dürr, J. pr. Chem. [2] 39, 283). Acetonechloroform is reduced by zinc-dust and alcohol, forming dichloro*iso*butylene, *iso*crotylchloride, and *iso*butylene (Jocitsch, J. Russ. Phys. Chem. Soc. 1898, 30, 920); and is decomposed by water at 180°, yielding hydrogen chloride and hydroxy*iso*butyric acid (Willgerodt, Ber. 1882, 15, 2305). By the action of benzene in presence of aluminium chloride the chlorine atoms of acetonechloroform are replaced wholly or in part by phenyl residues, and the compounds *diphenylchloromethyl dimethyl carbinol* $CPh_2Cl{\cdot}CMe_2{\cdot}OH$ b.p. 239°; *phenyldichloromethyl dimethyl carbinol* $CPhCl_2{\cdot}CMe_2{\cdot}OH$ b.p. 217°; and *triphenylmethyl dimethyl carbinol* $CPh_3{\cdot}CMe_2{\cdot}OH$ b.p. 260°, have been prepared, and similar compounds are obtained using toluene or *p*-xylene (Willgerodt, J. pr. Chem. [2] 37, 361).

Acetonechloroform is a powerful germicide, a satisfactory surgical dressing, and hypnotic for internal use (Aldrich and Houghton, Amer. J. Physiol. 1900, 3, 26); it is used as a specific for sea-sickness (Merck, Ann. Report,

1907, 1), and a 1–2 p.c. solution is used under the name of *anesin* for producing local anæsthesia (Cohn, Pharm. Zentr. H. 40, 33).

ACETONEDICARBOXYLIC ACID *v.* KETONES.

ACETONE OIL is the oily residue remaining after the separation of acetone from the products of the dry distillation of calcium acetate. It can also be prepared by the dry distillation of the lime salts obtained by neutralising fleece washings with milk of lime. About 15 litres of the oil are obtained from a cubic metre of fleece washings of 11°B. It is a slightly-coloured liquid of sp.gr. 0·835, having a penetrating smell and acrid burning taste. It consists mainly of methyl ethyl ketone (A. and P. Buisine, Compt. rend. 126, 351; 128, 561). According to Duchemin (Bull. Soc. chim. [3] 21, 798) acetone oil is of very variable composition, depending upon the nature of the pyrolignate from which it is prepared. A French Commission reported that it was effective as a denaturant of alcohol and it was adopted for this purpose by the Swiss Government in 1895.

For details of mode of manufacture from wool washings, *v.* Buisine (J. Soc. Chim. Ind. 18, 292; 21, 164); P. Baechlin, (Rev. Chim. Ind. 9, 112; 15, 240).

ACETONIC ACID *v.* HYDROXYBUTYRIC ACID.

ACETOPHENONE. *Phenyl methyl ketone. Hypnone* $C_6H_5{\cdot}CO{\cdot}CH_3$, is obtained by acting with benzoyl chloride on zinc methyl; by distilling a mixture of the calcium salts of benzoic and acetic acids; or by boiling together benzene and acetyl chloride with aluminium chloride. It can be isolated from the fraction of heavy oil of coal tar boiling at 160°–190° by addition of sulphuric acid, distilling the solution in steam and converting the distillate into the *p*-bromophenylhydrazone derivative of acetophenone (Weissgerber, Ber. 36, 754). It is best obtained synthetically by adding small quantities of sublimed ferric chloride (7 parts) to a mixture of benzene (5 parts) and acetyl chloride (7 parts) diluted with carbon disulphide. The mixture is then warmed on the water-bath, dried and fractionated (Nencki and Stoeber, Ber. 30, 1768).

Acetophenone crystallises in large plates, m.p. 20·5°; b.p. 202°. It possesses a persistent odour of oil of bitter almonds and cherry laurel water; is insoluble in water, but dissolves easily in alcohol, ether, chloroform, or benzene. It is readily oxidised by potassium permanganate to phenylglyoxylic acid (Glücksmann, Monatsh. 11, 246). By the action of ammonia on an alcoholic solution of acetophenone, the acetophenone ammonia is formed $CMePh(N:CMePh)_2$, m.p. 115° (Thomąe, Arch. Pharm. 244, 643) (*v.* KETONES).

Acetophenone forms a large number of derivatives and condensation products with aldehydes, halogens, acids, mercury salts, &c.

Acetophenone was discovered by Dujardin-Beaumetz and Bardet to possess powerful soporific properties (Compt. rend. 101, 960; Karmensky, Liss. Med. Chi. Acad. St. Petersburg, 1888–1889, No. 70). In quantities of 0·05 to 0·15 gram. it induces a quiet sleep, but is said to impart a disagreeable odour to the breath (Pharm. J. 1886, 582).

Aminoacetophenone (Camps, Arch. Pharm. 40, 15), b.p. 250°–252°; 135°/17 mm., has anæsthetic properties, which are not diminished by condensing it with aldehydes containing a phenolic hydroxyl, but are destroyed when it is condensed with benzaldehyde, tolualdehyde, or cinnamaldehyde (Hildebrandt, Chem. Zentr. 1905, ii. 502; Scholz and Huber, Ber. 37, 390; Schäfer, Ber. 39, 2181).

Acetophenonephenetidene, m.p. 88°, an antipyretic substance, can be obtained by heating molecular proportions of acetophenone and *p*-phenetidene *in vacuó*, then distilling *in vacuó* at 210°–212° (Valentiner, J. Chem. Soc. Ind. 15, 50; 17, 602).

β-ACETO-PROPIONIC ACID. *Lævulic acid*

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

This substance is formed by the action of dilute acids on a number of carbohydrates—*e.g.* levulose, inulin, galactose. It is also a product of oxidation of the terpene alcohols, but is best prepared by heating on the water-bath cane sugar with dilute hydrochloric acid (4 vols. water, 1 vol. conc. acid) until a brown flocculent precipitate is no longer formed. (Compare Tollens, Ber. 17, 668; Wehmer a. Tollens, Annalen, 243, 214.) The filtered liquid is then evaporated on the water-bath, extracted several times with ether, and after distilling off the ether the residue is fractionated in a vacuum.

It can be obtained by the hydrolysis of various nucleic acids (Kossel and Neumann, Zeitsch. physiol. Chem. 27, 2215; Inouye, *ibid.* 42, 117; Levene, *ibid.* 43, 119). For other methods of preparation, compare Tiemann and Semmler (Ber. 28, 2129); Verley (Bull. Soc. chim. [3] 17, 190); Erlenmeyer (J. pr. Chem. 179, 382); Blaise (Bull. Soc. chim. [3] 21, 647).

Lævulic acid crystallises in plates which melt at 33°. It boils at 239°, 148°–149°/15 mm. (Michael, J. pr. Chem. 152, 113), and has at 15° a sp.gr. 1·135. It is very soluble in water, alcohol, or ether, and is not attacked by bromine in the cold. Nitric acid converts it into carbon dioxide, acetic acid, succinic and oxalic acids. Iodine and sodium hydroxide form iodoform even in the cold. Hydriodic acid and phosphorus at 200° convert it into normal valeric acid; whereas sodium amalgam forms sodium γ-hydroxyvalerate acid in an alcoholic solution, and normal valeric acid in an acid solution. When added to boiling iodic acid solution diiodoacetoacrylic acid is formed (Angeli and Chiassi, Ber. 25, 2205). When placed over sulphuric acid in a vacuum it decomposes, leaving a residue of dihydroxyvaleric acid (Berthelot and André, Compt. rend. 123, 341).

The mercury salt $Hg(C_5H_7O_3)_2$, which crystallises in silvery plates, breaks up on treatment with sodium hydroxide, forming the two mercurilævulic acids $C_5H_6O_3Hg$ and $C_5H_4O_3Hg_2$. Lævulic acid readily condenses with benzil (Japp and Murray, Chem. Soc. Proc. 1896, 146), and with aldehydes (Meingast, Monatsh. 26, 265). It forms a semi-carbazone, m.p. 187° (Blaise, *l.c.*). The ethyl ester when treated with ethyl magnesium bromide yields a lactone, b.p. 105°–106°/18 mm. (Grignard, Compt. rend. 135, 627). Halogen substitution derivatives of lævulic acid have also been obtained (Wolff, Ber. 26, 2216; Wolff and Rüdel, Annalen, 294, 192; Conrad and Schmidt, Annalen, 285, 203).

The substance is employed on a manufac-

turing scale as a mordant instead of acetic acid, as it possesses the advantage of not being volatile with steam.

It is also used in the preparation of the antipyretic *antithermin*. Phenylhydrazine is dissolved in dilute acetic acid, and on adding a solution of lævulic acid a yellow precipitate is formed, which is purified by recrystallisation from alcohol (Pharm. J. [3] xvii. 801) (*v.* ANTITHERMIN).

ACETOPURPURINE *v.* AZO- COLOURING MATTERS.

ACETPHENETIDENE *v.* PHENACETIN.

ACETYLENE GROUP. Hydrocarbons having the general formula C_nH_{2n-2}.

The hydrocarbons of this series exist in two isomeric modifications. Representatives of the first group are

$CH:CH$ Acetylene. $CH_3{\cdot}C:CH$ Allylene.

And of the second

$CH_2:C:CH_2$ Isomeric allylene, $CH_2:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH:CH_2$ Diallyl.

The hydrocarbons of the first group thus contain the group $\equiv CH$ united to one carbon atom, and may be designated true acetylenes. They form compounds with copper and silver in which the hydrogen of the group (CH) is replaced by the metal.

When heated to a high temperature with alcoholic potash in a sealed tube the triple bond changes its position thus:

$C_2H_5{\cdot}CH_2{\cdot}C:CH \rightarrow C_2H_5{\cdot}C:C{\cdot}CH_3$.
$C_2H_5{\cdot}C:CH \rightarrow CH_3{\cdot}C:C{\cdot}CH_3$.

The reverse action occurs by boiling with metallic sodium.

The following general reactions yield hydrocarbons of this series:—

1. By heating the monohalogen derivatives of the hydrocarbons C_nH_{2n} with alcoholic potash

$CH_3{\cdot}CCl:CH_2+KOH=CH_3{\cdot}C:CH+KCl+H_2O$.

2. By the action of alcoholic potash on the dihalogen derivatives of the ethylene series. In this case the reaction takes place in two stages.

I. $CH_2Br{\cdot}CH_2Br+KOH = CHBr:CH_2+KBr+H_2O$.

II. $CHBr:CH_2+KOH=CH:CH+KBr+H_2O$.

The bromine derivatives give, as a rule, a better yield than the chlorides.

3. By electrolysing unsaturated dibasic acids.

$CH{\cdot}CO_2H:CH{\cdot}CO_2H=CH:CH+2CO_2+H_2$.
Fumaric acid — Acetylene

The acetylenes combine with Br_2 or Br_4; thus acetylene forms $C_2H_2Br_2$ and $C_2H_2Br_4$.

Nascent hydrogen converts the acetylenes into the hydrocarbons C_nH_{2n} and C_nH_{2n+2}.

The acetylenes in presence of mercuric bromide combine with water to form aldehydes and ketones (Kutscheroff, Ber. 14, 1542; 17, 28).

$C_2H_2+H_2O=C_2H_4O$
Acetylene. Aldehyde.

$CH_3{\cdot}C:CH+H_2O=CH_3{\cdot}CO{\cdot}CH_3$
Allylene. Acetone.

According to Desgrez (Ann. Chim. Phys. 1894, 3, 215; Bull. Soc. chim. [3] 11, 362), the elements of water can be made to combine directly with the acetylenes without the presence of condensing or other agents.

By polymerisation of the acetylenes, compounds of the benzene series are formed. Thus acetylene at a red heat yields benzene (Bone and Coward, Chem. Soc. Trans. 1908, 1197; Bone and Jerdan, Chem. Soc. Proc. 1901, 165 Maquenne, Compt. rend. 115, 558); allylene C_3H_4, by the action of sulphuric acid, gives mesitylene C_9H_{12} (trimethyl benzene); and crotonylene C_4H_6 gives hexamethyl benzene.

Acetylene C_2H_2 *i.e.* HC : CH is produced when an electric arc is formed between carbon points in an atmosphere of hydrogen (Bone and Jerdan, Chem. Soc. Trans. 1897, 54). Further, by passing the vapours of many carbon compounds (alcohol, ether, ethylene) through red-hot tubes (Bone and Coward, *l.c.*). It is also formed by electrolysing the sodium or potassium salt of fumaric or maleic acid, and by the action of silver, copper, or zinc-dust on iodoform (Cazeneuve, Compt. rend. 97, 1871). A steady stream of gas can be obtained by the action of the copper-zinc couple on bromoform (Cazeneuve, Compt. rend. 113, 1054).

By the action of water on the carbides of barium, calcium, or strontium (Travers, Chem. Soc. Proc. 1893, 15; Maquenne, *l.c.*; Moissan, Bull. Soc. chim. [3] 11, 1007).

By allowing the flame of a bunsen burner to strike back, or by the action of alcoholic potash on ethylene dibromide.

According to Matthews (J. Amer. Chem. Soc. 22, 106), a good laboratory method is to cover calcium carbide with absolute alcohol and add water drop by drop. The gas is purified by passing into copper sulphate solution acidulated with sulphuric acid, then over pumice stone saturated with an acetic or sulphuric acid solution of chromic acid.

Commercially acetylene is nearly always produced from calcium carbide (Lewes, J. Soc. Chem. Ind. 16, 33; Clowes, *ibid.* 209, 319; Wilson, *ibid.* 15, 103; Lüpke, Elektr. Chem. Zeit. 1895, 145; Wyatt, J. Soc. Chem. Ind. 14, 135; 796; 20, 109; Bamberger, Zeitsch. angew. Chem. 1898, 720). A rapid evolution of gas is also said to be obtained by treating calcium carbide with crystallised sodium carbonate previously mixed with powdered rock salt (J. Soc. Chem. Ind. 27, 438). Commercial acetylene often contains as impurities: ammonia, other hydrocarbons, carbon monoxide, hydrogen, nitrogen, oxygen, arsine, sulphuretted hydrogen, and phosphoretted hydrogen, the last of which is the most dangerous. The action of the gas on copper is due chiefly to these impurities. The gas can be purified and the impurities detected by passing it through cooled solutions of sulphuric acid, lime, lead or mercury salts, and chromic acid in sulphuric or acetic acid (Clowes, *l.c.*; Lunstroem, Chem. Zeit. 23, 180; Bergé and Reychler, Bull. Soc. chim. [3] 17, 218; Göttig, Ber. 32, 1879; Rossel and Landrisset, Zeit. angew. Chem. 1901, 77; Caro, J. Soc. Chem. Ind. 22, 17; 23, 15; Ullmann and Goldberg, Chem. Zentr. 1899, ii. 19; Pfeifer, J. f. Gasb. 42, 551; Frasuckel, Chem. Zentr. 1908, ii. 643; Eitner and Keppeler J. f. Gasb. 44, 548; Jaubert, J. Soc. Chem. Ind. 24, 116; Willgerodt, Ber. 28, 2107; Hoffmeister, Zeitsch. anorg. Chem. 48, 137).

The best method of freeing acetylene from phosphine is to pass the cooled gas over bleaching powder, or the compound $CaO,CaOCl_2,2H_2O$ or $CaO,CaOCl_2,H_2O$ (Ditz, D. R. P. 1906, 162324),

moistened with just sufficient water to make it cohere in balls, and finally over lime (Lunge and Cedercreutz, Zeitsch. angew Chem. 1897, 651; J. Soc. Chem. Ind. 16, 37; 24, 1294; 27, 798; Wolff, J. f. Gasb. 1898, 41, 683).

Acetylene is a colourless gas which, when quite pure, has a distinct and agreeable ethereal odour; it has no action on metals (Clowes, J. Soc. Chem. Ind. 16, 109; Moissan, Compt. rend. 121, 566), and is non-poisonous when inhaled in small quantities, although it may produce asphyxiation when more than 40 p.c. of it is present (Clowes, *l.c.*; Korda, Mon. Sci. 45, 409; Mosso and Ottolenghi, Ann. di Chim. e. di. Farmacol. 25, 163; Vitali, Chem. Zentr. 1898, ii. 586; Moissan, *l.c.*; Gréhaut, Compt. rend. 121, 564; Berthelot, *ibid.* 121, 566; Brociner, *ibid.* 121, 773; J. Soc. Chem. Ind. 16, 319; Rosemann, Chem. Zentr. 1895, ii. 998).

It condenses at 1° and 48 atm. to a colourless liquid which on rapid exhaustion solidifies; with water, liquid acetylene forms a crystalline hydrate $C_2H_2,6H_2O$ (Villard, Compt. rend. 120, 1262). With ozone acetylene is violently decomposed (Otto, Ann Chim. Phys. 1898, 13, 116). It explodes more violently than other hydrocarbons with oxygen (Meyer, Ber. 27, 2764; Chatelier, Compt. rend. 121, 1144; Gréhaut, *ibid.* 122, 832; Berthelot and Vieille, *ibid.* 123, 523; Bone and Cain, Chem. Soc. Proc. 1896, 176; Clowes, J. Soc. Chem. Ind. 15, 90, 418, 701, 891).

Any mixture with air containing 3–82 p.c. of acetylene is explosive (Bunte, Ber. 31, 5; Clowes, Chem. Soc. Proc. 1896, 143; Berthelot and Vieille, Compt. rend. 128, 177), but the explosibility is reduced by admixture with inert gases. It is slightly soluble in water, more so in alcohol or ether, and very readily so in acetone, with the last three of which, according to McIntosh (J. Phys. Chem. 1907, 306), it forms crystalline compounds.

Since acetylene gas, as well as the liquid, is highly explosive under pressure, it is best stored by solution in acetone (Berthelot and Vieille, Compt. rend. 123, 523; 124, 966, 988, 996, 1000; Claude and Hess, *ibid.* 124, 626; 128, 303; J. Soc. Chem. Ind. 20, 1021, 1196; 22, 288; 24, 191, 1101; 16, 788; Wolff, Zeitsch. angew. Chem. 1898, 919; Caro, J. Soc. Chem. Ind. 25, 1138).

The gas burns in air with a smoky flame, decomposes when exposed to sunlight, and forms condensation and resinous products when subjected to an electric discharge (Berthelot, Bull. Soc. chim. [3] 4, 480; Jackson and Laurie, Chem. Soc. Proc. 1906, 155; Losanitsch, Monatsh. 29, 753; Javitschitsch, *ibid.* 29, 1; Coehn, Zeit. f. Elektr. 7, 681; Billitzer, Monatsh. 23, 199; Schutzenberger, Compt. rend. 110, 889).

Acetylene is now used fairly extensively for illuminating purposes, and is a safe form of artificial lighting (Lüpke, Elektr. Z. 1895, 145; J. Soc. Chem. Ind., 16, 33; 18, 476, 343; Bullier, Bull. Soc. chim. [3] 17, 646) (*v. infra*). It is used in flashing-point tests (J. Soc. Chem. Ind. 1898, 949), and has been recommended by Lunstroem for freeing alcohol from water; by Violle (Compt. rend. 122, 79), for use in photometry; by Erdmann and Makowka (Zeitsch. anal. Chem. 46, 128) for the separation of copper from silver, alkaline earths, magnesium, aluminium, chromium, manganese, iron, nickel, cobalt, bismuth, antimony, arsenic, and tin (Makowka, Zeitsch. anal. Chem. 46, 145; Erdmann, *ibid.* 46, 125; Söderbaum, Ber. 30, 760, 814, 902, 3014).

Acetylene can be used as a starting-point for the production of alcohol (J. Soc. Chem. Ind. 1900, 476; Caro, *ibid.* 1895, 226), but the methods are costly and the yield poor. According to Vitali (L'Orosi, 21, 217), acetylene has considerable antiseptic properties.

Troubel (J. f. Gasb. 48, 1069) recommends the use of acetylene for autogenous soldering.

When acetylene is burned with compressed air or oxygen in a specially adapted glass-blower's lamp, a flame can be produced but slightly luminous, which is either oxidising or quite neutral, is comparable with the electric arc in intensity, and whilst capable of melting nickel, gold, and platinum, is free from the reducing and carburetting properties of the arc (Nichols, J. Soc. Chem. Ind. 20, 29).

On heating sodium in acetylene, hydrogen is given off, and the compounds C_2HNa and C_2Na_2 are formed (Matignon, Compt. rend. 124, 775; Skosarewsky, J. Russ. Phys. Chem. Soc. 36, 863; Moissan, Compt. rend. 126, 302). With the hydrides and ammoniums of the alkali metals and of calcium, compounds of the type $C_2M'_2$. C_2H_2 are formed (Moissan, Compt. rend. 127, 911; 136, 1217, 1522; 137, 463; Berthelot and Delépine, *ibid.* 129, 361).

The compounds with copper and silver correspond respectively with the formulæ $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$, or $C_2H_22Ag_2O$. The former is red, the latter yellowish. Both explode on heating (Blochmann, Annalen 173, 174; Kuntzmann, Bull. Soc. Chem. [3] 6, 422; Alexander, Ber. 32, 238; Isolva, *ibid.* 2697; Phillips, Amer. Chem. J. 16, 340; Scheiber and Flebbe, Ber. 41, 3816; Makowka, *ibid.* 824; Freund and Mai, Chem. Zentr. 1899, i. 410; Berthelot, Compt. rend. 132, 1525).

It also forms such compounds as $C_2H_2Cu_2Cl_2$, $C_2Ag_2AgNO_3$, and more complex ones still, some of which are very explosive (Chavastalon, Compt. rend. 124, 1364; 125, 245; 126, 1810; 127, 68; 130, 1634, 1764; 131, 48; 132, 1489; Hofmann and Küspert, Zeitsch. anorg. Chem. 15, 204; Söderbaum, Ber. 30, 760, 814; Willgerodt, Ber. 28, 2107; Arth, Compt. rend. 124, 1534; Berthelot and Delépine, *l.c.*; Nieuwland and Maguire, Amer. Chem. J. 28, 1025; Edwards and Hodgkinson, J. Soc. Chem. Ind. 23, 954; 25, 495; British Association Reports, 1904; Alexander, Ber. 32, 2381; Gooch and Baldwin, Zeitsch. anorg. Chem. 22, 235; Keiser, Amer. Chem. J. 14, 285).

Acetylene forms compounds with mercury of the type C_2Hg_2,H_2O; $3C_2Hg,H_2O$; $C_2(HgNO_3)_2$, many of which are very explosive (Nieuwald and Maguire, *l.c.*; Plimpton and Travers, Chem. Soc. Trans. 1894, 264; Keiser, *l.c.*; Plimpton, Chem. Soc. Proc. 1894, 32; Berge and Reychler, Bull. Soc. chim. [3] 17, 218; Peratoner, Gazz. chim. ital. 24, ii. 36; Gooch, *l.c.*; Alexander, *l.c.*; Hofmann, Ber. 31, 2212, 2783; Köthner, 2475; Burkard and Travers, Chem. Soc. Trans. 1902, 1270; Bilz and Mumm, Ber. 37, 4417; Brame, Chem. Soc. Trans. 1905, 427; Hofmann and Kirmreucher, Ber. 41, 314).

It also forms bromo-magnesium compounds,

HC : CMgBr; BrMgC : CMgBr (Oddo, Atti R. Acad. Lincei, 13, 187; Gazz. chim. ital. 38, i. 625).

With fuming sulphuric acid acetylene yields a sulphonic acid, and from the potassium salt $(C_2H_2)_3(SO_4KH)_4$ phenol can be obtained by treating with potash and distilling the product (Berthelot, Compt. rend. 127, 908; Schroeter, Ber. 31, 2189; Muthmann, *ibid.* 1880).

With fuming nitric acid, nitroform, certain neutral and acid compounds and the explosive substance $C_4H_2O_3N_4$, m.p. 78°, are obtained (Tustoni and Mascarelli, Atti Real. Acad. Lincei, 1901, 10, i. 442; Baschieri, Gazz. chim. ital. 31, i. 461; Mascarelli, *ibid.* 33, ii. 319).

With hydrogen peroxide acetylene is oxidised to acetic acid (Cross, Bevan, and Heiberg, Ber. 33, 2015).

Nascent hydrogen converts acetylene into ethylene and ethane.

When acetylene and hydrogen are passed over freshly-reduced nickel, cobalt, copper, or iron, or platinum black, ethane, ethylene, and liquid hydrocarbons are formed, in amounts depending on the nature of the metal, the relative proportions of acetylene and hydrogen, and the temperature of the reaction. When acetylene alone is passed over these metals, ethane, ethylene, hydrogen, and liquid paraffins, are formed, together with ethylenic and aromatic hydrocarbons, the proportion of the products formed depending on the catalyst and temperature. In the case of copper a greenish hydrocarbon—*cuprene* $(C_7H_8)_n$ is also formed; a similar compound is also obtained with nickel (Sabatier and Senderens, Compt. rend. 128, 1173; 130, 250, 1559, 1628; 131, 187; Moreau, *ibid.* 122, 1240).

A mixture of nitrogen and acetylene subjected to the action of induction sparks yields prussic acid: $C_2H_2+N_2=2HCN$ (Beilstein).

Chlorine and acetylene combine explosively when exposed to daylight, but according to Monneyrat (Compt. rend. 126, 1805), chlorine and acetylene in the absence of oxygen combine without explosion forming acetylene tetrachloride, which together with the dichloride, can also be produced by the action of acetylene on antimony pentachloride (Tompkins, D. R. P. 196324; J. Soc. Chem. Ind. 24, 150). The tetrachloride, which is an excellent solvent for fats, oils, and resins, can also be prepared by the action of acetylene and chlorine on acetylene dichloride when exposed to radium emanations (Lidholm, D. R. P. 1908, 201705). Acetylene can also be chlorinated by passing it into a mixture of sulphur chloride and a catalyst such as an iron compound (J. Soc. Chem. Ind. 24, 1255; 27, 643, 344; Nieuwald, Chem. Zentr. 1905, i. 1585).

Bromine added to an alcoholic solution of acetylene, or acetylene passed into bromine water, forms $C_2H_2Br_2$, but if the gas be passed through bromine the substances $C_2H_2Br_4$ and $(C_2HBr_3)_2$ are obtained (Gray, Chem. Soc. Trans. 1897, 1027; Elbs and Newmann, J. pr. Chem. [2] 58, 245); dibromoacetylene C_2Br_2, b.p. 76°–77°, is obtained by treating an alcoholic solution of tribromethylene with potash (Lemoult, Compt. rend. 136, 1333).

According to Keiser (Amer. Chem. J. 21, 261) when dry acetylene is gently warmed with solid iodine, two iodides are formed—a solid, m.p. 78°, liquid, b.p. 185° (Paternò and Peratoner, Gazz. chim. ital. 19, 580; 20, 670).

Acetylene diiodide $C_2I_2(C:CI_2$ Nef) is intensely poisonous (Loew, Zeit. Biol. 37, 222). According to Schenck and Litzendorff (Ber. 37, 3462), it can be used with benzene in making good photographic paper.

When subjected to the action of heat or light, C_2I_2 is changed into C_2I_4; with nitrous fumes it yields nitro-triiodoethylene $CI_2:CI.NO_2$, m.p. 107° (Meyer and Pemsel, Ber. 29, 1411; Bilz and Werner, Ber. 30, 1200; 33, 2190; Bilz and Küppers, Ber. 37, 4412; Chalmot, Amer. Chem. J. 19, 877; Nef, Annalen, 298, 202).

Mixed halogen derivatives have also been obtained (Lemoult, *l.c.*; Keiser, *l.c.*).

With water and carbon tetrachloride or similar halogen compounds at 0°, acetylene forms mixed crystalline hydrates (Forcrand and Thomas, Compt. rend. 125, 109).

Acetylene black, the soot produced when acetylene burns with a smoky flame or when it is exploded under two atmospheres pressure, may be used in the colour industry, calico-printing, and also in production of ink (J. Soc. Chem. Ind. 178, 711; 18, 284; 20, 955; Dépierre, *ibid.* 20, 890; Frank, Zeitsch. angew. Chem. 1905, 1733).

Allylene or **Allene** C_3H_4 exists in two isomeric modifications.

1. *Methyl acetylene or allylene* $CH_3{\cdot}C:CH$.

Is formed by the action of alcoholic potash on bromopropylene

$$CH_3:CBr:CH_2+KOH = CH_3{\cdot}C:CH+KBr+H_2O.$$

Also by acting with sodium on dichloracetone chloride

$$CH_3{\cdot}CCl_2{\cdot}CHCl_2+Na_4=CH_3{\cdot}C:CH+4NaCl.$$

Or by electrolysing the alkali salts of citraconic or mesaconic acids, or by action of magnesium on acetone vapour and treating the solid mass thus obtained with water (Keiser, Amer. Chem. J. 18, 328; Desgraz, Bull. Soc. Chem. [3] 11, 391; Lespieau and Chavanne, Compt. rend. 140, 1035).

Allylene is a colourless gas, b.p. −23·5°; m.p. −110°; very similar to acetylene, and, like it, forming compounds with metals. The mercuric compound $(C_3H_3)_2Hg$ is obtained by passing allylene through water containing mercuric oxide in suspension. It crystallises from hot alcohol in fine needles. It is soluble in hydrochloric acid with evolution of allylene, but does not explode on heating (Keiser, *l.c.*; Lossen and Dorno, Annalen, 342, 187; Plimpton and Travers, *l.c.*; Bilz and Mumm, *l.c.*; Hofmann, Ber. 37, 4459).

The silver compound $(C_3H_3)_2Ag$ forms microscopic needles which explode at about 150°.

According to Berthelot (Compt. rend. 126, 561, 567, 609, 616) allylene, when subjected to the silent electric discharge, condenses to a solid with a pungent empyreumatic odour; with nitrogen the substance $C_{15}H_{20}N$ is formed.

Allylene forms with bromine additive products, $C_3H_4Br_2$ and $C_3H_4Br_4$, and with halogen acids compounds of the type $CH_3{\cdot}CCl_2{\cdot}CH_3$. Concentrated sulphuric acid absorbs allylene readily and on distilling the solution with water, acetone, mesitylene, and allylenesulphonic acid

$C_3H_3SO_3H$ are formed (Schrohe, Ber. 8, 18 and 367). With hypochlorous and hypobromous acids, allylene forms dichlor- and dibrom-acetones, and trimethyl allylene yields the halogen pinacolins (Wittorf, Chem. Zeit. 23, 695).

2. *Symmetrical allylene or allene* $CH_2:C:CH_2$ is obtained by the action of sodium on β-chlorallylchloride

$$CHCl:CH\cdot CH_2Cl+2Na=CH_2:C:CH_2+2NaCl.$$

Or by the action of zinc-dust on an alcoholic solution of dibrompropylene (Gustavson and Demjanoff, J. pr. Chem. 1888, 201; Vaubel, Ber. 24, 1685; Lespieau and Chavanne, *l.c.*). And by the electrolysis of the alkali salts of itaconic acid.

The substance is a gas (b.p. −32°; m.p. −146°), but differs from unsymmetrical allylene in giving no precipitate with an ammoniacal copper or silver solution (Phillips, Amer. Chem. J. 16, 340). With aqueous mercuric chloride allene and its homologues yield white precipitates (Vaubel, *l.c.*; Lossen and Dorno, *l.c.*). It unites with bromine to form $C_3H_4Br_4$, b.p. 225°–230°, with decomposition.

According to Smirnoff (J. Russ. Phys. Chem. Soc. 35, 854; 36, 1184), the allene hydrocarbons can be identified by treatment with hypochlorous acid, when keto-alcohols of distinctive properties are obtained.

Butines C_4H_6.

Four isomerides exist.

1. *Ethylacetylene* $C_2H_5\cdot C:CH$. Formed by the action of alcoholic potash on $C_2H_5\cdot CCl_2\cdot CH_3$ (Bruylants, Ber. 8, 412).

By passing acetylene and ethylene through a red-hot tube (Berthelot, Ann. Chim. Phys. [4] 9, 466).

The compound is a liquid boiling at 18°, and is a true acetylene, since it forms precipitates with ammoniacal copper and silver solutions. With ammoniacal silver chloride and alcoholic silver nitrate it forms explosive compounds (Wislicenus and Schmidt, Annalen, 313, 221); it also yields a sodium derivative (Jociez, Chem. Zentr. 1897, i. 1012).

2. *Crotonylene* or *dimethylacetylene*

$$CH_3\cdot C:C\cdot CH_3,$$

Formed by acting with alcoholic potash on βγ-dibromobutane $CH_3\cdot CHBr\cdot CHBr\cdot CH_3$; by the action of sodium ethoxide on monobrompseudobutylene $MeCBr:CH\cdot CMe$ (Hölz, Annalen, 250, 230); or by the decomposition of the salts of β-bromoangelic acid (Wislicenus, Talbot, and Henge, Annalen, 313, 228). It is a liquid, b.p. 27·2°–27·6° (Wislicenus and Schmidt, *l.c.*). With bromine it forms a liquid $C_4H_6Br_2$, b.p. 146°–147° (Hölz, *l.c.*), and $C_4H_6Br_4$, which is solid, m.p. 243°; *iso*crotonylene dibromide, b.p. 149°–150°, is also known, and is not readily attacked by zinc-dust (Wislicenus and Schmidt, *l.c.*).

Crotonylic mono- and hydro-bromides, as well as the iodide and chloride derivatives, have also been obtained (Wislicenus, Talbot, and Henge, *l.c.*; Peratoner, Gazz. chim. ital. 22, ii. 86; Charon, Ann. Chim. Phys. 1899, 17, 228; Favorsky, J. pr. Chem. [2] 42, 143).

On shaking the hydrocarbon with sulphuric acid and water (3:1), hexamethylbenzene is obtained

$$3C_4H_6=C_{12}H_{18}=C_6(CH_3)_6.$$

3. *Vinyl-ethylene* $CH_2:CH\cdot CH:CH_2$ (Perkin and Simonsen, Chem. Soc. Trans. 1905, 857). Prepared by passing the vapours of fusel oil through a red-hot tube (Caventou, Annalen, 127, 348). It is present in compressed coal gas (Caventou, Ber. 6, 70), and in oil gas (Armstrong and Miller, Chem. Soc. Trans. 1886, 74). It gives no precipitate with an ammoniacal cuprous chloride solution. When treated with bromine in chloroform solution cooled to −21°, it gives a liquid dibromide, b.p. 74°–76°/26 mm., which at 100° is converted to a solid of the same composition, m.p. 53°–54°, b.p. 92°–93°/15 mm.; with bromine the liquid dibromide yields a tetrabromide (Griner, Compt. rend. 116, 273; 117, 553; Thiele, Annalen, 308, 333).

4. The *butine* $CH_3\cdot CH:C:CH_2$ is prepared by heating tetrachlorbutane with alcohol and the zinc-copper couple; or from chloral by treatment in the cold with zinc ethyl. It is a colourless liquid, b.p. 18°–19°, yields no precipitate with ammoniacal copper solutions, but with bromine yields di- and tetra-bromine derivatives (Norton and Noyes, Amer. Chem. J. 10, 430).

The compound $CH:C\cdot C:CH$, formed by the action of cupric chloride on copper acetylene, is described by Noyes and Tucker (Amer. Chem. J. 19, 123); pentachlorbutine C_4HCl_5 by Zincke and Kuster (Ber. 26, 2104).

Derivatives of the butines, some of which are used as dye-stuffs, are described by Freund (Ber. 34, 3109).

Pentines. Seven of eight possible pentines are known, of which *isoprene* obtained in the dry distillation of indiarubber is the most important (Ipatieff and Wittorff, J. pr. Chem. [2] 55, 1; Ipatieff, *ibid.* 4). It can be obtained synthetically by the action of alcoholic potash on β-dimethyltrimethylene dibromide. It has b.p. 33°–34°, unites with hydrogen bromide forming $CMe_2Br\cdot CH_2\cdot CH_2Br$, and has no action on ammoniacal cuprous chloride or silver nitrate (Euler, J. pr. Chem. [2] 57, 131).

When saturated with hydrogen chloride at 0° and then allowed to remain in a sealed tube at the ordinary temperature for two or three weeks, a substance analogous to indiarubber is formed (Bouchardt, J. Soc. Chem. Ind. 21, 56).

Two trimethylene pentines and *cyclo*pentine have also been obtained.

Of the higher terms of the series the *hexine diallyl* is of interest. It is formed by the action of sodium on allyl iodide

$$2CH_2:CH:CH_2I+2Na=CH_2:CH\cdot CH_2\cdot CH_2\cdot CH:CH_2+2NaI$$

also by distilling mercuric allyl iodide with potassium cyanide. It probably consists of a mixture of two isomerides (Wagner, Ber. 21, 3343; 22, 3056; Siderenko, J. Russ. Phys. Chem. Soc. 36, 898).

It forms a liquid smelling of horse-radish, boiling at 59°, and combines with bromine to form the tetrabromide $C_6H_{10}Br_4$, melting at 63°. If this be boiled with potash a liquid dibromodiallyl is obtained, which boils at 210°, and by the action of alcoholic potash yields *dipropargyl* C_6H_6, a liquid boiling at 85° isomeric with benzene, but having the constitution

$$CH:C\cdot CH_2\cdot CH_2\cdot C:CH.$$

ACETYLENE AS AN ILLUMINANT. Although acetylene was discovered by Davy as far back as 1836, its use as an illuminant became

practicable only in 1892, when Moissan in France, and T. L. Willson at Spray, showed that it was possible to make calcium carbide on a commercial scale in the electric furnace.

At temperatures above 3000° a mixture of lime and some form of carbon, such as coke, soot, anthracite, or charcoal, becomes semi-liquid, and reduction of the calcium oxide results with production of carbon monoxide and liberation of calcium, which unites with the excess of carbon to form calcium carbide:

$$\underset{\text{Lime.}}{2CaO} + \underset{\text{Carbon.}}{3C_2} = \underset{\text{Carbon monoxide.}}{2CO} + \underset{\text{Calcium carbide.}}{2CaC_2}$$

Water decomposes the carbide with reproduction of lime and generation of acetylene:

$$\underset{\text{Calcium carbide.}}{CaC_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Lime.}}{CaO} + \underset{\text{Acetylene.}}{C_2H_2}$$

In the early days of carbide manufacture little attention was paid to the purity of the materials, with the result that the compound formed contained impurities, some of which were decomposed by water and gave products contaminating the acetylene. Since the importance of purity in the acetylene has been recognised, everything possible is now done to reduce such impurities to a minimum.

The lime employed is burnt in special kilns heated by gas, as the ordinary method of lime-burning by means of coal, &c., introduces so many impurities into the finished material that a bad carbide results. The limestone from which the lime is obtained must be as free from foreign matter as possible for the same reason. The same restriction applies to the carbonaceous matter used as the source of the carbon, and it is of the utmost importance that the ash, sulphur, and phosphorus should be as low in quantity as possible.

The proportions of the lime and carbon required by theory are 56 parts of lime to 36 parts of carbon, but allowance has to be made for impurities and loss in manufacture, so that the ratio now adopted is 100 of lime to 70 of carbon, whilst in some cases, to ensure a more fusible product, a rather higher proportion of lime is used, but the carbide so made has a slightly inferior gas-generating power.

Various types of electric furnace have been devised for the manufacture of calcium carbide, but they can be divided practically into two classes: (*a*) those in which the arc is struck in a mass of the mixed lime and carbon placed round the poles, the upper pole being raised as the carbide is produced, thus gradually building up an 'ingot'; and (*b*) those in which the mixture is fed continuously between the carbon poles, the carbide remaining in the furnace in a fused condition, and being tapped from time to time, the product being known as 'run' carbide.

At the present time nearly all the European carbide is made by the latter process, whilst ingot carbide is still largely made in America, a rotary furnace of the 'Horry' type being much used, in which the slow revolution of the furnace removes the ingot as it is formed from the direct impact of the arc, and presents a fresh portion of the charge to its action.

For all practical purposes it may be stated that 1 E.h.p. per year will yield one ton of carbide. The size of the furnace in the case of the 'run' carbide is limited only by the size of the carbon electrodes that can be obtained; with 'ingot' carbide a furnace taking about 200 E.h.p. is the most useful, taking into consideration efficiency as well as wear and tear. The most usual current for such a furnace would be about 12 to 15 amperes per square inch of electrode surface at a pressure of 55–65 volts.

Cheap power is of course the main factor in the economical production of calcium carbide, and this has resulted in the carbide industry becoming localised in those districts where water power is available, but the important advances which have of late taken place in the development of power from gaseous fuel will probably result in the establishment of factories in localities where the necessary material can be readily obtained and a local market secured for the product, since carriage necessarily influences the cost of production.

The cost of production of calcium carbide may be taken as being about 7*l.* per ton under the most advantageous conditions.

Calcium carbide, as made in the electric furnace, is a dark crystalline substance with a metallic lustre, having a density of 2·22. The pure compound, however, has been produced by Moissan in thin white semi-transparent plates, the colour of the commercial material being due to the presence of iron and other impurities.

The impurities found in commercial carbide may be divided into those which can be decomposed by water, and those on which water has no action. Amongst the former are substances evolving phosphorus compounds on contact with water, aluminium sulphide, organic sulphur compounds and metallic nitrides: whilst the latter class contains such bodies as graphite, carbides of boron and silicon, carbides and silicides of various metals contained in the lime and in the ash of coke, these being left with the lime residue after the decomposition of the carbide by water, and in no way influencing the purity of the gas.

The purity of commercial acetylene depends primarily on the purity of the carbide from which it is generated, and as long as it is impossible to get absolutely pure materials for the manufacture of the carbide, so long will impurities be found in the gas made from it. The most important of these impurities are:

(*a*) Phosphoretted hydrogen, obtained from the decomposition of calcium phosphide, &c., by water, and, in burning with the acetylene, gives rise to phosphorus pentoxide, which forms a light haze in the room in which the gas is being burnt.

(*b*) Sulphuretted hydrogen, formed by the action of water on aluminium sulphide, &c., and yielding when burnt sulphur dioxide, which if dissolved by condensing moisture will absorb oxygen from the atmosphere, forming traces of sulphuric acid.

(c) Ammonia, from the magnesium nitride, which rapidly corrodes brass gas-fittings, and on burning produces traces of nitrogen acids.

Siliciuretted hydrogen is also found in small quantities in crude acetylene.

Several processes have been devised for the purification of acetylene by the removal of these compounds as well as of the hydrocarbon vapours formed by the polymerisation of the gas due to high temperature during generation,

The only impurity that offers any real difficulty in removal is the phosphoretted hydrogen, and three substances have been suggested and used in practice for this purpose: (*a*) bleaching powder, (*b*) acid copper or iron salts, and (*c*) acid solution of chromic acid.

The bleaching powder is employed in the form of small lumps, as offering the least resistance to the flow of the gas when in a slightly moistened state. Its action is purely that of oxidation, the phosphoretted and sulphuretted hydrogen being converted respectively into phosphoric and sulphuric acids, the acetylene being unaffected. To obtain as large a surface as possible the bleaching powder is sometimes mixed with an inert body, such as sawdust or oxide of iron, but in whatever condition the bleaching powder is used the gas requires an after-purification for the elimination of chlorine compounds, for which purpose a lime purifier is generally employed.

Bleaching powder, though an efficient purifying agent when in good order, is apt to be uncertain in its action, and cases have frequently occurred of spontaneous firing and explosion when air has been admitted to purifiers containing this material that have been in use for some time, so that precautions are necessary when using this method of purification.

An acid solution of cuprous chloride, or solids made by impregnating kieselgühr or similar porous bodies with the acid copper salt, are also very effective in removing the various impurities, the phosphorus and sulphur compounds being transformed into copper phosphide and sulphide. The disadvantages of the process are that a second purification with lime is required to remove acid vapours, and that the material being highly acid cannot be used in ordinary metal containers, whilst if the copper salt became neutralised by ammonia there might be danger of the explosive copper acetylide being formed. Under suitable conditions 1 kilogram of the material will purify 20 to 25 cubic metres of the gas, the acetylene not being acted upon, and the action being regular and certain.

Chromic acid in solution containing sulphuric or acetic acid, or kieselgühr charged with this mixture, is the third purifying agent, and eliminates the phosphoretted and sulphuretted hydrogen and the ammonia. When exhausted the spent material can be regenerated by exposure to the air.

In practice these three materials seem to give equally good results, and the passage of the gas through the solution or solid scrubs out of it to a great extent the tarry fog and lime dust often mechanically held in the gas when it has been generated too rapidly or at too high a temperature.

Absolute purification is by no means necessary; for ordinary use all that is required being to reduce the amount of impurity below the limit at which the products of combustion are injurious to health or cause haze; and with a fairly pure specimen of carbide mechanical scrubbing is sufficient if a generator of the non-automatic type is employed, and the gas is stored in a holder before use.

When calcium carbide is acted upon by water the changes that take place may be represented by the equations:—

$$\underset{\text{Calcium carbide.}}{CaC_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Lime.}}{CaO} + \underset{\text{Acetylene.}}{C_2H_2}$$

$$\underset{\text{Lime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium hydroxide.}}{Ca(HO)_2}.$$

And so great is the affinity of the carbide for water that the calcium hydroxide so formed is slowly decomposed on standing by any excess of the carbide.

The first generator was of the simplest construction, the carbide being contained in a glazed vessel provided with two side tubulures and a lid that could be clamped down gas-tight. Through one of the tubulures water was admitted by means of a siphon, whilst the gas evolved was led through the other tubulure to a holder, but when the commercial possibilities of the gas had become apparent, inventors at once turned their attention to the multiplication of the forms of generator.

Although the generation of acetylene by thus bringing calcium carbide in contact with water seems so simple, yet in actual practice it was complicated by several difficulties, amongst which may be mentioned the heat of the reaction, which caused the polymerisation of some of the acetylene, and by the fact that the evolution of gas did not cease immediately the water supply was cut off, this being due to water mechanically held in the residue formed, to the dehydration of the calcium hydroxide by the unchanged carbide, as well as to the moisture condensed from the gas as the temperature of the generator fell.

Acetylene generators can be divided into two main classes—those in which water is brought in contact with the carbide, the latter being in excess; and those in which the carbide is thrown into water, the water being always in excess. The first class may be subdivided into those in which water is allowed to rise to the carbide, those in which it drips on to the carbide, and those in which a vessel full of carbide is lowered into water and then withdrawn as the generation of the gas becomes excessive.

Each of these types may be 'automatic' or 'non-automatic.' In the former are to be found devices for regulating and stopping at will the generation of the gas within limits, whilst the 'non-automatic' variety aim at developing the gas from the carbide with as little loss as possible and storing it in a holder.

The points to be aimed at in a good generator are:

(*a*) Low temperature of generation.

(*b*) Complete decomposition of the carbide.

(*c*) Maximum evolution of gas from carbide used.

(*d*) Low pressure in every part of the apparatus.

(*e*) Removal of all air from the apparatus before collection of the gas.

Generators of the 'drip' type, in which water is allowed to fall slowly upon a mass of carbide, possess most of the disadvantages due to heat of generation, fluctuation of pressure, &c., and this type has been abandoned except for the smallest forms of portable generator. Those in which water rises to the carbide are most efficient, and overheating can be avoided by ensuring that the water never rises above that portion of the carbide which is undergoing decomposition: in other words, that the gas

leaves the carbide immediately upon its formation and passes away to the holder with the least opportunity for becoming overheated by contact with decomposing carbide.

Generators in which the carbide dips into water and is then withdrawn are apt to overheat to a dangerous extent, especially if the generator be over-driven.

Although it might be expected that the dropping of the carbide into an excess of water would produce the coolest and purest gas, yet this is not the fact, and evidence of overheating of the gas is often found in generators of this class, as a coating of lime can form around the lumps, preventing the free access of water, and allowing the interior of the mass from which generation is proceeding to become heated to redness; the efficiency also is very low, as a considerable amount of the gas is dissolved in its upward passage through the large volume of water.

Theoretically 64 parts by weight of carbide require only 36 parts by weight of water for complete decomposition and conversion of the lime into hydroxide, but it is found in practice that, owing to the heat of the reaction driving off some of the water as steam, and a further portion mechanically adhering to the slaked lime, double this amount of water is necessary, and the only safe way to ensure entire decomposition of the carbide is to add sufficient water to flood the residue.

When acetylene is burnt in air under such conditions as to complete its combustion, it is converted into carbon dioxide and water vapour, the same compounds that are produced by all combustible hydrocarbons, 1 cubic foot of the gas requiring 2½ cubic feet of oxygen, or five times that amount of air.

When acetylene was first used for illuminating purposes, Bray union jet burners were employed, and although a very high duty was obtained, the pressures necessitated were too high to be desirable, and carbon was rapidly deposited on the burner tip, and caused such serious smoking of the flame as to considerably prejudice the use of the new illuminant. The proper combustion of any hydrocarbon gas, however rich in carbon, can be effected by supplying the flame with exactly the amount of air necessary to prevent smoking, and it is under these conditions that the highest illuminating effect possible with a particular burner is obtained. The ratio between the air to be supplied and the gas consumed depends upon the thickness of the flame and the pressure at which the gas issues from the burner.

If acetylene be burnt from a 000 Bray union jet burner at ordinary pressure a smoky flame is obtained, but if the pressure be increased to 4 inches an intensely brilliant flame results, free from smoke and giving an illuminating value of 240 candles per 5 cubic feet of gas consumed. For practical purposes, however, this pressure is too high, and the largest burners at first adopted, which required the consumption of 1 cubic foot of acetylene per hour, gave on an average 32 candles at an inch pressure.

These first burners were of the union jet type, in which very fine holes were employed for the delivery of the gas, and drilled at a more obtuse angle than ordinarily used for coal gas, thus causing a greater insuck of air into the flame, and ensuring a more complete combustion. Some specially small union jet burners were also produced by Bray, and both these nipples answered extremely well for a time and developed from 30 to 36 candle power per cubic foot of gas consumed, but they both had the same weakness, and after a few hundred hours began to smoke, and evolve copious clouds of soot-flakes.

This trouble generally began by a filiform growth of carbon appearing on the jet of the burner, which quickly distorted the flame, impeding proper combustion and causing the formation of quantities of free carbon. If the burner was cleaned and relighted, the trouble began again in an hour or two, and the only remedy was to replace the burner by a new one.

The smoking of acetylene burners after they have been in use for some little time, more particularly if the gas be turned down, is due indirectly to the property possessed by acetylene, in common with many heavy gaseous hydrocarbon compounds, of polymerising as the temperature rises; and also to the pressure at the burner-tip being insufficient to impart to the gas the velocity necessary to ensure the admixture with sufficient oxygen to effect its complete combustion; or, in some cases to the flow of gas through the burner holes being checked by accumulation of foreign matter therein.

If the steatite jet of a burner in which smoking has developed be broken it will be found to be carbonised for some depth into the material, showing that a liquid hydrocarbon has soaked into the steatite and has been decomposed by heat with deposition of carbon. The generally accepted idea is that the heat of the burner polymerised some of the acetylene to benzene, and that this scrubbed out by friction at the nipple led to the carbonisation and choking of the burner. Another theory, however, is that the heat evolved by the reaction between the carbide and water in the generation of the gas polymerises some of the acetylene immediately upon its formation, and that a certain quantity of the liquid hydrocarbon so formed is held in suspension and carried by the gas as a vapour to the burner, where it is scrubbed out by frictional contact and gradually accumulates there and is decomposed.

Although the deposition of carbonaceous matter does not take place so readily in burners supplied with gas that has been generated slowly and at a low temperature with subsequent washing and purification, yet it is a fact that the trouble arises when the gas is in the purest possible condition. Gas generated below 280° will not so frequently give rise to the trouble of carbonising at the burner, but if this temperature be exceeded in generation, no after-treatment of the gas will prevent it.

A small percentage of water carried along with the gas mechanically, or a little lime dust held in suspension, is also a source of carbon deposit at the burner.

Carbonisation of the burner is aggravated by 'turning down,' in which case the flow of gas is checked and the flame plays about the tip of the burner, heating it to a temperature favourable to polymerisation, when carbon is deposited, and by its catalytic action causes the

accumulation of further growths. If, however, the gas is burned at full pressure, the flame is not in actual contact with the burner, and the velocity of the issuing jet of gas induces currents of air around and through it, which prevent the temperature of the burner being raised to a degree sufficient to polymerise the gas to any material extent.

For the above reasons it was soon discovered that ordinary gas burners of the union jet pattern were unsuitable, although attempts had been made in America to use acetylene diluted with a certain proportion of air, which permitted it to be burnt in flat flame burners, but the danger of such admixture being recognised efforts in this direction were soon abandoned.

In France burners were devised in which jets of acetylene coming from two tubes spaced some little distance apart were made to impinge and splay each other out into a flat flame, whilst soon after Bullier introduced the idea of sucking air into the flame at or just below the burner-tip.

No real advance, however, was made in burners for acetylene until 1896–97, when Bullier's principle of making the tips of the burner jets into small bunsens was adopted by Dolan in America, and Billwiller on the Continent.

The Billwiller burner has two steatite arms rising at right angles from a common base from which the acetylene issued at two small orifices exactly opposite each other and giving the double jet. Immediately above the gas orifice a small platinum plate was fixed at a distance of about 0·5 mm. from the steatite, with a hole in it rather larger than the orifice in the steatite just below. The acetylene issuing from the hole in the steatite rushed through the hole in the platinum above and drew air in under the platinum plate. The air so drawn in flowed to the confines of the rapidly travelling stream of acetylene and passed upwards around it, so preventing contact between the edge of the hole in the platinum and the acetylene, whilst the metal, being part of a collar of platinum fixed round each steatite arm, and being a good conductor of heat, prevented such heating as would lead to the deposition of carbon from the gas.

FIG. 1.

These burners, made by Schwarz of Nuremberg, and sold under the name of the 'Basle' burner, gave excellent results, as is shown in the following table :—

Number of burner	Gas consumed (cub. ft.)	Pressure in inches (water)	Total light (candles)	Candles per cub. ft. of gas
1	0·35	2·25	4·2	12·0
2	0·625	2·25	19·0	30·4
3	0·75	3·0	24·0	32·0
4	0·90	3·0	32·0	35·5
5	1·00	3·0	36·0	36·0
6	1·00	3·0	40·0	40·0

In 1897 Dolan in America made a burner on the same principle as the Billwiller burner, though of slightly different construction. It consisted of a metal base, the upright from which forked into two arms, which near their extremities were bent inwards at right angles. These arms carried steatite or 'lava' tips, bored with a fine hole from the interior to the base of the mushroom head, where its diameter was more than doubled, whilst four small lateral air tubes were bored at regular intervals from the base of the head to the broad aperture of the nipple, with the result that the flow of acetylene from the narrow into the wider tube sucked air in through the side tubes and surrounded the ascending gas with an envelope which prevented its contact with the heated tip. These burners, which are more generally known as the 'Naphey' burners, gave very good results, and have been more widely adopted than the Billwiller burners that preceded them, partly because they did away with the expense of the platinum, were cheaper to make, and were less liable to break.

These tips were very largely manufactured on the Continent, both the American and English supply coming from Nuremberg. The form of mounting, however, was considerably varied in order to suit the taste of the user or to give the burner a new name. In one very popular form the arms are made as a portion of a circle, this modification doing away with the friction and check to the flow of gas due to the sharp bend in the original pattern, whilst these again are made up in groups of two or three burners where greater illumination is required.

The great drawback to all the Naphey tip burners is that the heat from the flame causes a slight and gradual warping of the metal mounting, with the result that after a time the jets become slightly thrown out of their true position, which at once distorts the flame and causes it to throw up smoky points. This trouble is not found with burners having steatite or composition arms, as these, being pressed or cut, do not warp with the heat.

These burners proved the forerunner of a host of others in all of which the same principle was adopted, one of the simplest and most popular being shown in Fig. 2, whilst Fig. 3 is a section

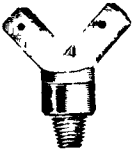


FIG. 2.

FIG. 3.

of the same burner, showing the construction and air inlets.

Although these burners possess many advantages and can be used for several hundred hours without smoking, they have the drawback that the flame cannot be turned down, as, after the flame has been left turned down for an hour or two, it will be found that it will generally start smoking when the normal consumption is restored.

In order to overcome this trouble Bray introduced a burner in which, by placing a second air-supply chamber of larger dimensions above the first, such a complete encircling of the jet of gas by air was ensured that the variations

in gas pressure caused by turning down the flame do not lead to carbonisation.

The same principle is utilised by Schwarz in the 'Suprema' burner made at Nuremberg, which is shown in Fig. 4.

Another burner has been brought out by this maker in which the idea of air injection has been successfully adapted to a slit burner: the gas issues from a series of fine holes placed below a cap provided with a broad slit

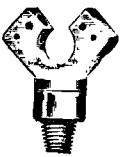


FIG. 4.

FIG. 5.

and side air tubulure, the gas drawing in sufficient air in its passage through the slit to prevent smoking or carbonisation of the burner (Fig. 5).

From the earliest introduction of acetylene attempts have been made to utilise it with incandescent mantles, but under the pressures which are usually obtained from the ordinary generating apparatus this has not proved successful. Acetylene, when consumed in an atmospheric burner, gives an excessively hot flame, not only on account of its composition, but also from its endothermic character. Several difficulties, however, are met with in trying to burn acetylene mixed with air in sufficient proportion to yield a non-luminous flame, namely:

(*a*) The wide range over which such mixtures are explosive.

(*b*) The low temperature of ignition.

(*c*) The high speed at which the explosive wave travels through the mixture of gas and air.

In order to make a bunsen burner for acetylene the tube has to be very narrow, and even then flashing back is very liable to occur, whilst a high pressure is needed to bring about a satisfactory mixture of the gas with sufficient air to ensure combustion with an absolutely non-luminous flame. The range of explosibility lies between 3 p.c. and 82 p.c. of acetylene in the mixture, and the propagation of the explosive wave cannot be stopped by the ordinary device of using wire gauze, on account of the low ignition point of the mixtures. By using a tube ½ mm. in diameter the explosion ceases to be propagated at all, but such tubes, on account of their small diameter, cannot be utilised singly. The difficulty can be surmounted by using a bundle of small tubes united to form a single burner, or by employing a large tube having a constriction at one point of not more than 5 mm. diameter. The diameter of the tube at the constriction must be in a definite proportion to the particular mixture of air and acetylene consumed, as the more air the greater must be the constriction in the strangulated portion of the tube, owing to the increased velocity of the explosive wave.

With an acetylene bunsen, and using a Welsbach No. 2 mantle, as much as 90 candles per cubic foot of acetylene has been obtained. It may be taken that when used with a mantle acetylene will give double the illuminating power per cubic foot as compared with the light obtained when the gas is burnt in the ordinary acetylene flat-flame burners under the best conditions, but very widely different results have been obtained, owing to irregularities in the pressure or lack of air regulation, and at the moment of lighting or turning out there is a liability of a small but violent explosion, which has disastrous effects upon the mantle. A further difficulty is caused when phosphoretted hydrogen is present as an impurity, for this leads to the formation of fusible phosphates of thorium and cerium, with consequent destruction of the mantle. Apart from these considerations, the mantle appears to be hardened and strengthened by the intense heat to which it is subjected, but it is not yet determined how the life of the mantle is affected by the temperature of the flame.

Under the light yielded by the combustion of acetylene colours appear practically the same as in daylight, and all tints and shades can be as clearly distinguished from one another as in sunlight. For this reason the gas has been found to be of invaluable utility in dyeing and colour printing. The spectrum of acetylene, however, although the same as that of daylight for red and yellow, has an increase in the blue rays of 0·46, which brings them to about the same value as the Northern Light. The violet rays show a slight increase, so that acetylene is even richer than sunlight in the rays which are so essential to the chemical action of light, and yet the red rays which are so detrimental in colour work do not predominate, as in the electric arc.

In 1896 Claude and Hess, in France, suggested the idea of making use of the solubility of acetylene in certain liquids as a means of storing this gas, and acetone was tried as the solvent. But it was found that the simple solution of acetylene in acetone, although less liable than the compressed or liquefied acetylene to explosion, could not be said to be sufficiently free from danger to admit of its general use. It was soon discovered by Janet and Fouche that when acetylene is dissolved in acetone absorbed by porous material of the right kind under 10 atmospheres pressure, it was impossible to produce explosion. The medium employed has a porosity of 80 p.c. soaked with 43 p.c. of the capacity of the cylinder with acetone. In this way one cubic foot of cylinder space can be made to hold 100 cubic feet of acetylene, which is, to a large extent, given off when the tap of the cylinder is opened.

Acetone dissolves 24 times its volume of acetylene at 15° and under ordinary atmospheric pressure, the solubility increasing with the augmentation of pressure, and the volume of the acetone also increasing very largely. Under 12 atmospheres 300 volumes of gas are dissolved.

The oxy-acetylene flame has within the last few years become of great service in autogenous welding. The advantages of such a flame were well recognised previous to 1901, but considerable difficulty was experienced in providing a blowpipe which would consume the acetylene at low pressures, and it was not until the introduction of dissolved acetylene that success was attained. Blowpipes are now made in which the oxygen alone is under pressure, the acetylene being under the low pressure as

delivered from a generator. The two systems are known as the high-pressure and low-pressure methods of oxy-acetylene welding.

The temperature of the oxy-acetylene flame is approximately 3000°, and from the nature of the combustion the flame has a reducing action tending to exclude the possibility of oxidation of the metals undergoing treatment. Theoretically 2·5 volumes of oxygen are required for each volume of acetylene, but in practice it is found that the proportions are approximately 1·4 to 1·0, this low proportion of oxygen ensuring a reducing action in the flame.

In the high-pressure system the oxygen is delivered from an ordinary cylinder under pressure, and the acetylene, dissolved in acetone under pressure, is also supplied from cylinders. Both cylinders are fitted with special governors, as a perfect regulation of the flame is one of the main secrets of success.

With the low-pressure plant the acetylene is made in an ordinary generator, which may be of the automatic or non-automatic type, the size of the works to a great extent influencing the kind of generator used, but, whatever type be adopted, it is necessary that the generation of the gas should not be accompanied by overheating, as this leads to low temperatures at the burner and other troubles. The gas should be purified before use, as the presence of the phosphoretted and sulphuretted hydrogen would tend to spoil the weld, and the purifying agent should be renewed when necessary. After leaving the purifiers the gas is distributed to the various points in the workshops in gas- or steam-barrel piping, and at each point a hydraulic back-pressure valve is inserted, in order to prevent the oxygen through any mischance flowing back through the acetylene service. The first successful blowpipe was the Fouche, employed with the low-pressure system, and this type has held its own in spite of the competition of other patterns. After the weld has been made the plate is annealed, this being essential. Although the results of tests up to the present are not very consistent, it may be taken that, on the average, the welded joint has a tensile strength from 95 to 80 p.c., depending on the thickness of the plate.

There are many classes of work in which oxy-acetylene welding can be advantageously employed. In the motor-car industry, both in the garage and repair shop, it has proved of great service, it being a comparatively simple matter, for instance, to mend a cracked cylinder or gear-box. For the welding of tubes, repairs to boilers *in situ* needed by corrosion, &c., for the mending of fractured stems and stern posts, the process has been invaluable.

Acetylene has been found of great service in the illumination of small towns and country villages, and for isolated houses and farms. It has been employed in photography on account of its richness in actinic rays. For headlights on motors, for train lighting, for buoys, and in fact in a number of cases where bright and trustworthy light is required without the complication of a coal-gas works or the dangers of oil, acetylene has proved its worth.

It has been found that the rays from an acetylene light possess remarkable penetrative powers in fog or mist, being in this respect superior to the arc light or incandescent mantle. V. B. L.

ACHRODEXTRIN *v.* DEXTRIN.

ACHYRANTHES ASPERA or *Aghara*. An Indian plant used as a simple and as a remedy for toothache.

ACID ALBUMEN *v.* PROTEINS.

ACID ALIZARIN, -BLUE, -GREEN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ACID CERISE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACID GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACIDIMETRY and ALKALIMETRY. This branch of quantitative analysis dealing with the estimation of acids and alkalis is of great technical importance. In pure aqueous solutions the amount of acid or alkali can usually be ascertained with considerable accuracy by determining the specific gravity of the liquid at a definite temperature and referring to a table especially drawn up for this purpose.

Direct estimations may also be made by suitable gravimetric methods, but volumetric processes are almost exclusively employed, and are indeed the only methods available for distinguishing between free and combined acid or alkali. In these operations the quantity of acid or alkali present is calculated from the amount of standard alkali or acid required respectively to neutralise it exactly, the precise point of neutralisation being determined by the addition of a small quantity of an *indicator*, *i.e.* a substance which by undergoing a marked change of colour renders evident the transition from acidity to alkalinity, or *vice versâ*.

Indicators. Although many natural and artificial colouring matters have been recommended as indicators, comparatively few are actually used, those most frequently employed being *methyl orange*, *phenolphthalein*, and *litmus*.

Artificial indicators are either very weak organic acids or (more rarely) weak bases, and the prevalent view regarding their behaviour is that in solution their colour in the non-ionised state differs from that which they exhibit in the ionic condition.

In accordance with the ionic theory of solution, a very weak acid HM exists in solution, mainly, but not entirely, in the non-ionised state, the equilibrium between ions and undissociated molecules $HM \rightleftharpoons \overset{+}{H} + \overset{-}{M}$ being expressed quantitatively by the equation

$$\overset{-}{M} \times \overset{+}{H}/HM = \text{constant}$$

in which the symbols denote the molecular concentrations of the ions and molecules, and where as in the case under discussion $\overset{-}{M}$ and $\overset{+}{H}$ are very small in comparison with HM.

Any increase in the value of $\overset{+}{H}$, which is effected by adding a small quantity of a fairly strong (ionised) acid to the solution, leads to a corresponding diminution in the value of $\overset{-}{M}$. The reverse change, leading to an increase in the value of $\overset{-}{M}$, with a corresponding decrease in the value of $\overset{+}{H}$, is effected by adding a slight amount of a fairly strong (ionised) alkali hy-

droxide, since the equilibrium $\overset{+}{H} \times \overset{-}{OH} = \text{constant}$ obtains in aqueous solutions, and the alkali added increases considerably the value of the factor $\overset{-}{OH}$. If the acid HM and the ion M differ in colour, then, in any solution containing this acid a change from acidity to alkalinity, *i.e.* from a state in which $\overset{+}{H}$ predominates over $\overset{-}{OH}$ to the reverse condition, may be indicated by an appreciable change of colour. The degree of ionic dissociation of the indicator HM must, however, be considerably smaller than that of either acid or alkali employed in the titration; moreover, another acid HR, having a smaller degree of ionisation than HM, will indicate the transition with even greater precision, providing that the recognition of the colour-change is not more difficult. The quantity of indicator employed must be so small that the amount of alkali required to neutralise it is negligible.

For Theory of Indicators, *v.* Ostwald (Scientific Foundations of Analytical Chemistry, translated by McGowan), Küster (Zeitsch. anorg. Chem. 1897, 13, 127), Waddell (J. Phys. Chem. 1898, 2, 171), Vaillant (Compt. rend. 1903, 136, 1192), Stieglitz (J. Amer. Chem. Soc. 1903, 25, 1112; Amer. Chem. J. 1908, 39, 651; 1909, 42, 115), McKoy (Amer. Chem. J. 1904, 31, 503), Hewitt (Analyst, 1908, 33, 85), Salm (Zeitsch. physical. Chem. 1906, 57, 471; Zeitsch. Elek. Chem. 1907, 13, 125), Salessky (Zeitsch. Elek. Chem. 1904, 10, 204), Fels (Zeitsch. Elek. Chem. 1904, 10, 208), Schoorl (Chem. Zentr. 1907, i. 300, 502, 585), Hantzsch (Ber. 1907, 40, 1556; 1908, 41, 1187), Rohland (Ber. 1907, 40, 2172), Acree (Amer. Chem. J. 1908, 39, 528, 649, 789), Handa (Ber. 1909, 42, 3179); and *cf.* Noyes for the physico-chemical theory (J. Amer. Chem. Soc. 1910, 32, 815).

Indicators may be divided broadly into three classes: (i.) Those insensitive to very weak acids, such as carbonic, boric, and hydrosulphuric acids; these indicators comprise among others *methyl orange*, *lacmoid*, *cochineal*, and *iodoeosin*. (ii.) Those somewhat sensitive to weak acids, although as a rule these acids cannot be accurately titrated with their aid; if weak volatile acids such as carbonic acid are removed by boiling, these indicators act like those of the first class towards fairly strong acids and bases. *Litmus* is the chief representative of this group. (iii.) Those highly sensitive even to weak acids. This class contains *phenolphthalein*, *turmeric*, and *rosolic acid* (*v.* Glaser, Zeitsch. anal. Chem. 1899, 38, 273; Wagner, Zeitsch. anorg. Chem. 1901, 27, 138).

The more important indicators are described below in alphabetical order.

Aurin (*Commercial or para-Rosolic acid*) is a mixture of several substances, produced by heating together phenol and oxalic and sulphuric acids; it appears in commerce in yellowish-brown resinous lumps. A 1 p.c. solution in 60 p.c. alcohol is employed, 0·5 c.c. being added to the solution to be titrated. In acid solution the colour is pale *yellow*, in alkaline solution *rose-red*. This indicator is very sensitive and well adapted for titrating barium hydroxide solutions, but it is affected by carbon dioxide and hydrogen sulphide.

Cochineal. The colouring matter in the product obtained from the dried female insect *Coccus cacti* (Linn.), is termed *carminic acid*. The best trade product, which is called 'silver cochineal,' was first recommended as an indicator by Luckow (J. pr. Chem. 1861, 84, 424; Zeitsch. anal. Chem. 1862, 1, 386); 3 grams of the substance (not pulverised) is extracted with 250 c.c. of dilute alcohol (1 vol. alcohol: 3–4 vols. water), and the clear liquid decanted. In alkaline solution the colour is *violet*, in acid *yellowish-red*. This indicator, which is very sensitive to strong acids and bases, is extremely useful in titrating ammonia; it is scarcely affected by carbon dioxide. The colour-change is well defined even in artificial light. Cochineal is, however, useless for titrating organic acids; and iron, aluminium and copper salts must be absent, since their solutions remain pink even when acid.

Curcumin (*Turmeric yellow*). The colouring matter from the roots of *Curcuma longa* (Linn.), is turned *yellow* by acids and *reddish-brown* by alkalis; it is nearly always employed as a *test-paper*, and is useful in detecting ammonia and boric acid.

Gallein (*Alizarin violet*, *Pyrogallolphthalein*). This compound, prepared by heating together pyrogallol and phthalic anhydride (Baeyer, Ber. 1871, 4, 457, 555, 663), was proposed as an indicator by Dechan (Pharm. J. 15, 849). A 0·1 p.c. alcoholic solution is used, 10 drops being added to 100 c.c. of liquid. In alkaline solution the colour is *reddish-violet*, in acid *pale-brown*. This indicator is scarcely affected by carbon dioxide, and can be used in the accurate titration of organic acids.

Iodoeosin (*Tetraiodofluorescein*, *Erythrosin B.*). This substance, prepared by iodating fluorescein, is a brick-red powder soluble in hot alcohol or in ether, but almost insoluble in water or cold alcohol; it was first recommended by Mylius and Förster (Ber. 1891, 24, 1482); 0·5 gram of the sodium derivative of iodoeosin is dissolved in 1 litre of water, 2·5 c.c. are added to the solution to be titrated together with 5 c.c. of chloroform, the mixture being shaken in a stoppered bottle during titration. While alkaline the aqueous layer is *rose red*, when acid the aqueous layer becomes *colourless*, and the chloroform assumes a yellowish tint (Ellms, J. Amer. Chem. Soc. 1899, 21, 359; M. and F. used ether instead of chloroform). With this indicator, centinormal or even millinormal solutions can be titrated; it is indifferent to carbon dioxide, and phosphoric acid can be titrated as a monobasic acid with sodium hydroxide (Glücksmann, Chem. Zentr. 1902, (i.) 1131). Feeble bases, such as the alkaloids, may also be titrated, using iodoeosin as indicator.

Lacmoid (*Resorcin Blue*). This substance is obtained by heating gradually to 110° a mixture of 100 parts of resorcinol, 5 parts of sodium nitrite, and 5 parts of water. When the violent reaction moderates, the mass is heated to 115°–120° until evolution of ammonia ceases. The product is a glistening reddish powder (Traub and Hock, Ber. 1884, 17, 2615).

A 0·3 p.c. alcoholic solution is employed; a better colour change is produced if 5 *grams* of naphthol green are dissolved in a litre of this solution (Zeitsch. angew. Chem. 1890, 3, 163). In alkaline solution the colour is *blue*; in acid, *red*. Although these colour changes resemble

those of litmus, the indicator is more closely allied to methyl orange. It is only slightly affected by carbon dioxide, although direct titration of carbonates is not satisfactory in cold solution; lacmoid test paper may, however, be used in almost any experiment for which methyl orange is suitable. This indicator is useless for organic acids.

Litmus occurs in commerce in the form of small cubical granules mixed with a large proportion of calcium carbonate. An aqueous solution of this product not only contains free alkali, but also a variable proportion of colouring matters which interfere with the delicacy of the reaction. Special precautions must therefore be taken in preparing the solution for use in acidimetry. Various processes have been recommended by Berthelot and De Fleurieu (Ann. Chim. Phys. 1865, [4] 5, 189), Wartha (Ber. 1876, 9, 217), Mohr (Titrirmethode), Luttke (Zeitsch. anal. Chem. 1892, 31, 692). The following method gives excellent results: The litmus is extracted three or four times with boiling methylated alcohol of 85 p.c. in order to remove the injurious colouring matters, the residue is extracted with cold water, slightly acidified with sulphuric acid, and boiled to expel carbon dioxide. The extract is neutralised with baryta water, a few bubbles of carbon dioxide passed in to remove excess of baryta, and the liquid again boiled and filtered. The solution should contain about 20 grams of solid matter per litre, and must be kept in vessels to which the air has free access. If kept in closed vessels it undergoes fermentation and is decolourised. The colour is restored when the liquid is exposed to air. The colour of the solution should be *purple*; it turns *blue* with alkalis, and *red* with acids, and is affected by carbon dioxide, sulphur dioxide, and hydrogen sulphide. (For the relative merits of litmus and methyl orange, *v.* Reinitzer, Zeitsch. angew. Chem. 1894, 547, 574; Lunge, *ibid.* 1894, 733.)

The colour change is rendered more delicate by conducting the titration in the monochromatic light obtained by heating a bead of sodium carbonate in a bunsen flame (L. Henry, Compt. rend. 1873, 76, 222). The red solution seems colourless, whilst the blue solution is almost black. Litmus is not well adapted for use by gas- or lamp-light.

Luteol. The preparation of this substance, a hydroxychlorodiphenylquinoxaline, is described by Autenrieth (Arch. Pharm. 1895, 233, 43), and by Glaess and Bernard (Mon. Sci. 1900, 14, 809); it forms fine, woolly, yellowish needles, m.p. 246°. A 0·33 p.c. alcoholic solution is used as an indicator. In alkaline solution the colour is *yellow*; in acid it is *colourless*. This indicator is said to be remarkably sensitive, excelling Nessler's solution as a test for ammonia; but it is sensitive to carbon dioxide (Higgins, J. Soc. Chem. Ind. 1900, 19, 958). It was especially recommended by Autenrieth for use in Kjehldahl's process (*v.* ANALYSIS).

Methyl orange (*Helianthin, Poirrier's Orange III.*). This substance, prepared by diazotising sulphanilic acid and coupling the resulting diazonium salt with dimethylaniline, was introduced as an indicator by Lunge (Ber. 1878, 11, 1944; J. Soc. Chem. Ind. 1882, 1, 16). One gram of pure methyl orange (either the free acid or its sodium salt) is dissolved in 1 litre of water, and two drops of this solution are added in each titration; if, owing to dilution during the titration, the colour becomes too faint, another drop of the indicator is added; on no account should too much indicator be used, since the colour change, from *yellow* in alkaline to *pink* in acid solution, is not sharp in such circumstances. Methyl orange is exceedingly useful, since its indications are practically unaffected by the presence of carbonic, hydrosulphuric, boric, and silicic acids; carbonates and sulphides may therefore be titrated in cold solution as if they were hydroxides. All titrations must be made with this indicator in cold aqueous solution, and, since methyl orange is not very sensitive as compared with various other indicators, the acid or alkali employed should be fairly concentrated. It is advisable to employ normal solutions, though with N/2 or even N/5 solutions it is possible to determine an end-point to within a single drop. With N/10 solutions, especially when carbonates are being titrated, there is a distinct *brownish* transition tint between the yellow and pink, and results may be uncertain to the extent of one or two drops (*cf.* Küster, Zeitsch. anorg. Chem. 1897, 13, 140).

The addition of indigo-carmine to methyl orange has been recommended by Luther (Chem. Zeit. 1907, 31, 1172), who states that the colour change is very pronounced. Ethyl orange is stated by Wieland to be even better than methyl orange (Ber. 1883, 16, 1989).

Methyl red. This substance, prepared by diazotising anthranilic acid and coupling the resulting diazonium salt with dimethylaniline, was introduced as an indicator by Rupp and Loose (Ber. 1908, 41, 3905). A 0·2 p.c. alcoholic solution is employed, and two drops of this are added in each titration. The colour change is from a pure *yellow* in alkaline to a *reddish-violet* in acid solution, and is very pronounced. This indicator is very sensitive, and can be used for titrating weak bases in centinormal solution. The precise extent to which it is affected by carbon dioxide has not yet been determined; but ordinary sodium hydroxide solutions containing a little carbonate can be accurately titrated in the cold.

Phenacetolin, first recommended by Degener (Zeit. d. Ver. f. d. Rübenzucker Industrie, 1881, 357; J. Soc. Chem. Ind. 1882, 1, 85), is prepared by boiling together for several hours molecular proportions of phenol, acetic anhydride, and sulphuric acid. The product is extracted with water to remove excess of acid, dried and dissolved in alcohol in the proportion of 1 gram to 500 c.c. It is *pale yellow* with alkalis, *red* with carbonates of the alkalis and alkaline earths, *colourless* or *pale yellow* with acids. It is used for estimating both hydroxide and carbonate when present in the same solution.

Phenolphthaleïn, obtained by heating phenol with phthalic anhydride and concentrated sulphuric acid (Baeyer, Annalen, 1880, 202, 69), was proposed as an indicator by Luck (Zeitsch. anal. Chem. 1877, 16, 322). One or two drops of a 0·5 p.c. alcoholic solution are used in each titration. In alkaline solution the colour is *red*; the acid solution is *colourless*. Owing to its very weak acid character, phenolphthaleïn is the indicator *par excellence* for organic acids; it

is useless, however, in the presence of ammonium salts, and since even carbonic and hydrosulphuric acids discharge the red colour, it is necessary to work with solutions free from these acids or titrate in boiling solution; hence its use is somewhat restricted. A convenient method of titrating organic acids with ordinary sodium hydroxide solutions using phenolphthaleïn as indicator, is described by Philip (Chem. Soc. Trans. 1905, 87, 991); *cf.* McCoy (Amer. Chem. J. 1904, 31, 503); and Schmatolla (Ber. 1902, 35, 3905).

Turmeric *v.* CURCUMIN.

Many other indicators have been proposed from time to time, among others the following:—

Alizarin (Schaal, Ber. 1873, 6, 1180); *Alizarin-red* 1. W.S. (Knowles, J. Soc. Dyers, 1907, 23, 120); *Congo-red*; *cyanine* (Schönbein, J. pr. Chem. 1865, 95, 449); *cyanogen iodide* (Kastle and Clark, Amer. Chem. J. 1903, 30, 87); *diaminazoatoluenesulphonic acid* (Troeger and Hille, J. pr. Chem. 1903, 68, 297); *ferric salicylate* (Weiske, J. pr. Chem. 1875, 12, 157; Wolff, Compt. rend. 1900, 130, 1128; Gerock, Chem. Zentr. 1900, ii. 1294); *flavescin* (Lux, Zeitsch. anal. Chem. 1880, 19, 457); *fluorescein* (Krüger, Ber. 1876, 9, 1572; Zellner, Chem. Zeit. Rep. 1901, 25, 40); *hæmatoxylin* (Wildenstein, Zeitsch. anal. Chem. 1863, 2, 9); *metanil yellow* (Linder, J. Soc. Chem. Ind. 1908, 27, 485); *methyl-3-aminoquinoline* (Stark, Ber. 1907, 40, 3434); *extract of mimosa flowers* (Robin, Compt. rend. 1904, 138, 1046); *para-nitrophenol* (Langbeck, Chem. News, 1881, 43, 161; Spiegel, Ber. 1900, 33, 2640; Zeitsch. angew. Chem. 1904, 17, 715; Goldberg and Naumann, Zeitsch. angew. Chem. 1903, 16, 644); *paranitrobenzeneazo-α-naphthol* (Hewitt, Analyst, 1908, 33, 85); and *Poirrier's blue* C4B (Engel, Compt. rend. 1886, 102, 214).

The relative sensitiveness of the more important indicators and their behaviour under various conditions have been investigated by Wieland (Ber. 1883, 16, 1989), and especially by Thomson (Chem. News, 1883, 47, 123, 135, 184; 1884, 49, 32, 38, 119; 1885, 52, 18, 29), whose results are summarised in the following table:—

—	Litmus	Lacmoid	Aurin	Methyl orange	Phenacetolin	Phenolphthaleïn
Sensitiveness	0·05	0·01	0·01	0·05	0·01	0·01
Hot solutions	Available	Available	—	—	—	—
Ammonia	Available	Available	Available	Available	Available	Not available
Ammonium salts	Not affected	Not affected	Lesssensitive	Lesssensitive	Not affected	Not available
Neutral alkaline salts	Not affected	Not affected	Not affected	Lesssensitive	Not affected	Not affected
Carbon dioxide	Indefinite	Indefinite	Indefinite	Not affected	Colour changed	Indefinite
Hydrogen sulphide	Indefinite	Decolourised	Indefinite	Not affected	Not affected	Indefinite
Alkaline carbonates	Indefinite	Indefinite	Indefinite	Alkaline	Red colour	Alkaline
Alkaline bicarbonates	Indefinite	Indefinite	Indefinite	Alkaline	—	Neutral
Sulphites	Indefinite	Alkaline	Neutral	Alkaline	Not available	Neutral
Acid sulphites	Indefinite	Neutral	Acid	Neutral	Not available	Acid
Silicic acid	Neutral	Neutral	Neutral	Neutral	Neutral	Not available
Alumina	Indefinite	Alkaline	Indefinite	Alkaline	Neutral	Neutral
Boric acid	Indefinite	Indefinite	Indefinite	Neutral	Indefinite	Indefinite
Sodium thiosulphate	Neutral	Neutral	Neutral	Neutral	Neutral	Neutral
Sulphides	Alkaline	Not available	—	Alkaline	Alkaline	Alkaline
Hydrosulphides	Indefinite	Not available	—	Alkaline	—	Neutral
Potassium nitrite	Neutral	—	Neutral	Destroyed	Neutral	Neutral
Oxalic acid	Available	Not available	Available	Not available	Not available	Available
Phosphoric acid	Indefinite	Monobasic	Indefinite	Monobasic	Indefinite	Dibasic
Arsenic acid	Indefinite	Monobasic	Indefinite	Monobasic	Monobasic	Dibasic
Arsenious acid	Neutral	Neutral	Indefinite	Neutral	Neutral	Indefinite
Phenol	Neutral	Neutral	Neutral	Neutral	Neutral	Indefinite

The sensitiveness is measured in c.c. of decinormal acid required to produce a distinct change when the volume of the liquid is 100 c.c. It should be borne in mind, however, that the sensitiveness of many indicators changes (usually diminishes) in the presence of considerable quantities of dissolved salts. Where a reaction is given as 'indefinite,' it is not meant that there is no effect, but that the change is not sufficiently sharp to be available in analysis. In many cases where the reaction is indefinite in cold solutions it becomes definite if the liquid is boiled, *e.g.* litmus with sulphides, sulphites, and carbonates; phenolphthaleïn with sulphides and carbonates. Lacmoid is most serviceable in the form of paper, and several of the reactions which are unsatisfactory with the solution are sharp and distinct with the paper, *e.g.* with carbonates, sulphides, and sulphites.

Gawalowski recommends (Zeitsch. anal. Chem. 1883, 22, 397) the use of a mixture of methyl orange and phenolphthaleïn, which is deep-red with excess of alkali, pale-yellow when neutral, and rose-red with excess of acid. Compare also Schlotz (Zeitsch. Elek. Chem. 1904, 10, 549) on mixed indicators.

Preparation of Standard Acids and Alkalis.

Standard solutions of acids and alkalis are usually prepared on the *normal* basis, the *normal* solution of a chemical reagent containing one gram-equivalent of the substance in one litre of the solution (*v.* ANALYSIS, Volumetric section).

In acidimetry and alkalimetry it is essential to have a standard solution of some acid or alkali, the concentration of which is known with great accuracy; this solution serves to standardise the others. Various suggestions have been made, but the general choice, at least for technical purposes, has fallen on hydrochloric acid as the standard acid; sulphuric acid is frequently employed and, less often, oxalic acid.

The commonest method of fixing the exact concentration of the hydrochloric (or sulphuric) acid consists in titrating the acid against weighed amounts of pure anhydrous sodium carbonate, a process originally employed by Gay-Lussac, and strongly recommended by Lunge, Sutton, and Treadwell. Separate weighed quantities of the pure carbonate are dissolved in 50–100 c.c. of cold distilled water, and each titrated with the acid, using methyl orange as indicator. The

concentration of the acid solution is calculated from each result, and the mean of the concordant values adopted as correct. Chemically pure sodium carbonate is obtainable in commerce, and should be free from all but traces of chloride and sulphate; it is dried in a platinum crucible with continual stirring for 20–30 minutes at such a temperature that the crucible bottom is barely red hot, or the crucible, embedded in sand, may be heated at 300° for half an hour. Pure sodium carbonate may also be prepared by heating the bicarbonate at a temperature not exceeding 300° (Lunge, Zeitsch. angew. Chem. 1897, 10, 522). Sulphates and chlorides are removed from the bicarbonate by washing with cold water. (For the preparation of pure sodium bicarbonate, *v.* Reinitzer (Zeitsch. angew. Chem. 1894, 7, 551), and North and Blakey (J. Soc. Chem. Ind. 1905, 24, 396).)

The foregoing method, although extensively used, has been adversely criticised, the chief objection being that it is impossible to dehydrate the carbonate or bicarbonate without losing a little too much carbon dioxide. It is asserted that sodium oxide is present even when the temperature of drying has not exceeded 170°; *v.* Kissing (Zeitsch. angew. Chem. 1890, 3, 262); Higgins (J. Soc. Chem. Ind. 1900, 19, 958); Sörensen and Andersen (Zeitsch. anal. Chem. 1905, 44, 156); North and Blakey (J. Soc. Chem. Ind. 1905, 24, 396); Sebelin (Chem. Zeit. 1905, 29, 638); but *cf.* Seyda (Chem. Zentr. 1899, (i.) 1164); Lunge (Zeitsch. anal. Chem. 1904, 17, 231; 1905, 18, 1520).

A satisfactory method of checking the values obtained by the carbonate method depends on the fact that sodium oxalate, when heated, is converted into sodium carbonate. As this oxalate can be prepared in a high degree of purity, the residue of carbonate theoretically obtainable from a known weight of oxalate can be calculated, and the presence of any sodium oxide is immaterial providing that all calculations are based on the original weight of sodium oxalate.

The weighed oxalate is carefully heated in a platinum crucible until all the separated carbon has been burnt off and the residual carbonate begins to fuse; the cooled residue is dissolved in water and titrated as already described; *v.* Sörensen (Zeitsch. anal. Chem. 1897, 36, 639; 1903, 42, 333, 512; 1905, 44, 156), Lunge (Zeitsch. angew. Chem. 1905, 18, 1520); and ANALYSIS, (Volumetric section, standardisation of permanganate).

From time to time many other standards have been proposed, and among others the following:—

Potassium tetroxalate; succinic acid (Phelps and Hubbard, Zeitsch. anorg. Chem. 1907, 53, 361; Phelps and Weed, *ibid.* 1908, 59, 114, 120); *borax* (Rimbach, Ber. 1893, 26, 171); *potassium hydrogen tartrate* (Borntrager, Zeitsch. anal. Chem. 1892, 31, 43); *potassium dichromate* (Richter, Zeitsch. anal. Chem. 1882, 21, 205); *potassium iodate* (Fessel, Zeitsch. anal. Chem. 1899, 38, 449); *potassium biiodate* (Meineke, Chem. Zeit. 1895, 19, 2); *sodium* (Hartley, Chem. Soc. Trans. 1873, 26, 123; Neitzel, Zeitsch. anal. Chem. 1893, 32, 422; *cf.* Hopkins, J. Amer. Chem. Soc. 1901, 23, 727); and *sulphuric acid*, prepared by electrolysing copper sulphate solution (Hart and Croasdale, Chem. News, 1891, 63, 93; Kohn, J. Soc. Chem. Ind. 1900, 19, 962).

Hydrochloric acid. In preparing a normal solution advantage may be taken of the fact that an aqueous solution of hydrogen chloride which boils at a constant temperature has a practically constant composition. A quantity of ordinary concentrated acid is distilled from a capacious retort until one-third has passed over. The residual liquid will contain 20·2 p.c. of hydrogen chloride, and 165 c.c. when diluted to 1 litre will form an almost exactly normal solution; it should be standardised by one of the following processes.

The strong acid is diluted until its specific gravity is approximately 1·1, and distilled; after three-fourths of liquid have passed over, the remaining distillate is collected apart, and the barometric height observed. The final quarter of the distillate is of perfectly definite composition, and the following table gives the actual content of hydrogen chloride for a definite barometric height, together with the weight of distillate which contains one gram-equivalent of hydrogen chloride, *i.e.* which yields a normal solution when diluted to 1 litre:—

Barometer	%HCl	Grams of mixture containing 1 mol. HCl
770	20·218	180·390
760	20·242	180·170
750	20·266	179·960
740	20·290	179·745
730	20·314	179·530

These results were calculated from the observed weights of liquid, without reduction to vacuum standard; the compositions were determined gravimetrically by precipitation as silver chloride (Hulett and Bonner, J. Amer. Chem. Soc. 1909, 31, 390).

The simplest method of preparing a large quantity of nearly normal hydrochloric acid is to find the approximate composition of the ordinary concentrated acid by taking its specific gravity with a hydrometer and referring to a suitable table; the requisite quantity of the acid is then measured out and appropriately diluted with distilled water.

To standardise the solution, it is titrated against successive weighed quantities of pure sodium carbonate (or sodium oxalate), as described above. Each separate amount of carbonate should weigh from 2·0 to 2·5 grams, in order to ensure a burette reading of 40 to 50 c.c. It is best to use methyl orange for indicator, since the titrations can be rapidly and accurately carried out in the cold; if litmus is used, the titration must be made in boiling solution. In the latter case, it is quicker to add a measured excess of acid to the carbonate, and titrate back with sodium hydroxide the value of which is known in terms of the acid; but the titration must nevertheless be done in boiling solution. The calculation is very simple: if x grams of sodium carbonate require y c.c. of hydrochloric acid, then 1 c.c. acid $= x/y$ grams of sodium carbonate. Now, 1 c.c. N-acid $=0{\cdot}05300$ grams sodium carbonate, and hence concentration of acid $= \frac{x}{0{\cdot}053y}$ times normal $=z$ times normal, say. As a rule, this is a very

convenient method of expressing the result; *e.g.* if the acid is used to estimate an alkali of equivalent e, then 1 c.c. acid $= \frac{e}{1000} \times z$ grams of alkali. If necessary, the acid solution may be diluted with distilled water so that the ratio final volume ÷ initial volume $= z$; it will then be exactly normal. A simple arithmetical calculation is required, and if this process is contemplated, care should be taken initially to ensure that z shall be slightly greater than unity.

Hydrochloric acid is most accurately standardised gravimetrically by precipitating chlorine with excess of silver nitrate and weighing the silver chloride in a Gooch crucible. The solution may be titrated against pure silver according to the Mint process for assaying this metal. The method may be modified by adding the silver solution in very slight excess, this excess being determined in the filtrate with N/10-thiocyanate (Thorpe's Quantitative Analysis; Dittmar's Quantitative Analysis; Knorr, J. Amer. Chem. Soc. 1897, 19, 814; Hopkins, *ibid.* 1901, 23, 727). These methods are trustworthy only when the hydrochloric acid is free from chlorides.

A simple and accurate process of standardisation consists in immersing weighed pieces of Iceland spar in a measured volume of the acid, and noting the loss in weight of the spar after the acid is neutralised (Masson, Chem. News, 1900, 81, 73; Green, *ibid.* 1903, 87, 5; *cf.* Thiele and Richter, Zeitsch. angew. Chem. 1900, 13, 486).

Small quantities of standard hydrochloric acid may be prepared by absorbing dry hydrogen chloride in a weighed quantity of water and ascertaining the increase in weight (Moody, Chem. Soc. Trans. 1898, 73, 658; Higgins, J. Soc. Chem. Ind. 1900, 19, 958; Acree and Brunel, Amer. Chem. J. 1906, 36, 117).

Sulphuric acid. An approximately normal solution is obtained by diluting to 1 litre 28 c.c. of pure concentrated sulphuric acid (sp.gr. 1·84).

The solution may be standardised with pure sodium carbonate or oxalate (*v.* HYDROCHLORIC ACID), or a measured quantity treated with a slight excess of ammonia, evaporated to dryness, and the residual ammonium sulphate heated at 120° and weighed. This method gives trustworthy results only when pure redistilled acid is employed in preparing the solution (Weinig, Zeitsch. angew. Chem. 1892, 5, 204; Shiver, J. Amer. Chem. Soc. 1895, 17, 351; Hopkins, *ibid.* 1901, 23, 727; Marboutin and Pécoul, Bull. Soc. chim. 1897, 17, 880).

A measured volume of the acid is added to a weighed excess of sodium carbonate in a platinum dish, the solution evaporated, the residue dried at 300° and weighed. The change in weight due to the transformation of sodium carbonate into sulphate indicates the amount of acid present in the solution. This method is much preferable to precipitating and weighing the acid as barium sulphate (*cf.* Richardson, J. Soc. Chem. Ind. 1907, 26, 78).

Sulphuric acid solutions of definite concentration may be prepared by specific gravity measurements (Pickering, Chem. Soc. Trans. 1890, 57, 64). A quantity of the purest acid is diluted with half its volume of water, and the specific gravity of the mixture accurately determined at 15° or 18° in a Sprengel pyknometer. The percentage of sulphuric acid in the solution is then obtained by reference to tables giving the values for 15°/15° or 18°/18° (*v.* Sutton's Volumetric Analysis, 9th ed., or J. Soc. Chem. Ind. 1899, 18, 4). The table given in J. Soc. Chem. Ind. 1902, 21, 1511, may be employed when the specific gravity (15°/15°) has been calculated without introducing any vacuum corrections, which must be allowed for if the other tables are employed. Between the limits of 66 p.c. and 81 p.c. the following formulæ reproduce the values in the tables with an error not exceeding 0·04 p.c.:—

$$P = 86\ S_{15} - 69{\cdot}00$$
$$P = 86\ S_{18} - 68{\cdot}82$$

where P = percentage of sulphuric acid, and S_{15} and S_{18} = the specific gravities referred to water at 15° and 18° respectively, calculated without allowing for 'air displaced' (Marshall, J. Soc. Chem. Ind. 1899, 18, 4). The diluted acid may be kept in a stoppered bottle without change, and by weighing out the appropriate amount and diluting to a litre, a normal solution of sulphuric acid can be rapidly prepared.

Oxalic acid. A normal solution is prepared by dissolving 63·03 grams of the recrystallised hydrated acid $H_2C_2O_4 + 2H_2O$ in water and diluting to 1000 c.c. As the crystallised acid is somewhat effloresent, especially on slightly warming, it may contain less than two molecular proportions of water. The solution may be checked against a standard alkali, using phenolphthaleïn as indicator, or against an accurately standardised permanganate solution (*cf.* Treadwell-Hall, Analytical Chemistry, vol. 2).

Oxalic acid solutions do not keep very well.

Sodium hydroxide. To prepare a normal solution, clear transparent lumps of the best white commercial caustic soda are selected, any opaque portions of their surface scraped off, and 50 grams of the substance weighed out for each litre of solution. The cooled solution is standardised against the standard hydrochloric acid, using methyl orange as indicator, and taking 50 c.c. for each titration.

For the preparation of sodium hydroxide solutions free from carbonate, *v.* Küster (Zeitsch. anorg. Chem. 1897, 13, 134; 1904, 41, 472, and Bousfield and Lowry, Phil. Trans. 1905, 204, 253).

Potassium hydroxide *cf.* SODIUM HYDROXIDE.

Barium hydroxide. An approximately N/10-solution is best prepared from the crystalline hydroxide $Ba(OH)_2, 6H_2O$. The powdered substance is shaken with distilled water, the solution allowed to settle, the clear liquid siphoned off and diluted with an equal volume of recently boiled-out water. The solution must be kept permanently in contact with that portion already in the burette, and guard tubes are required to prevent access of carbon dioxide. The solution is standardised against succinic acid, phenolphthaleïn being used as indicator; or a measured volume may be evaporated to dryness with a slight excess of pure sulphuric acid, the residual barium sulphate being gently heated and weighed.

The chief use of this solution is in titrating organic acids, using phenolphthaleïn as indicator. For this purpose carbon dioxide must be excluded, and barium hydroxide is consequently the most convenient alkali to employ.

Ammonia. This solution is not often employed; an approximately semi-normal solution, readily obtained by diluting 28 c.c. of concentrated ammonia solution to 1 litre, is titrated against hydrochloric acid in the cold, using methyl orange as indicator; phenolphthaleïn cannot be employed.

Schultze has determined the rates of expansion of normal solutions of acids and alkalis and other solutions employed in volumetric analysis (Zeitsch. anal. Chem. 1882, 21, 170). The following are the results for average temperatures :—

—	Oxalic acid	Hydrochloric acid	Nitric acid
0°	10000	10000	10000
10°	10010	10010	10018
15°	10019	10019	10031
20°	10031	10030	10045
25°	10046	10043	10061

—	Sulphuric acid	Potassium hydroxide	Sodium hydroxide
0°	10000	10000	10000
10°	10017	10019	10021
15°	10029	10031	10034
20°	10044	10046	10048
25°	10060	10062	10065

Typical Acidimetric and Alkalimetric Estimations.

Determination of total alkali. A weighed quantity of the substance (10 grams) is dissolved in water, filtered if necessary, and diluted to 500 c.c.; 50 c.c. are withdrawn, mixed with a measured excess (25 c.c.) of normal acid, boiled gently for ten minutes to expel carbon dioxide, and the excess of acid determined with standard alkali. The volume of standard acid *minus* the excess of acid gives the volume of acid required to neutralise the total alkali, *i.e.* the alkali present as hydroxide, carbonate, sulphide, sulphite, thiosulphate, aluminate, and silicate. If methyl orange is used as indicator, boiling is unnecessary, and the alkaline solution is titrated directly with standard acid. If direct titration with litmus as indicator is preferred, the solution must be continuously boiled during the titration.

Alkaline hydroxide in presence of carbonate. 100 c.c. of the above solution are heated, mixed with excess of barium chloride, allowed to cool, diluted to 250 c.c. and well shaken. When the precipitate has settled, 50 c.c. of the clear liquid are withdrawn and titrated with standard acid. The quantity of acid used × 25 gives the volume equivalent to the hydroxide in the weight of substance originally taken. The reaction which takes place is expressed by the equation

$$x\mathrm{M_2CO_3} + y\mathrm{MOH} + (x + \tfrac{y}{2})\mathrm{BaCl_2}$$

$$= x\mathrm{BaCO_3} + \tfrac{y}{2}\mathrm{BaH_2O_2} + (2x + y)\mathrm{MCl}.$$

The barium carbonate is precipitated and a quantity of barium hydroxide equivalent to the alkaline hydroxide remains in solution. The solution cannot be filtered, since the barium hydroxide would absorb carbon dioxide from the air with formation of the insoluble carbonate.

In order to avoid error due to the presence of the precipitate, and to economise time, Watson Smith (J. Soc. Chem. Ind. 1882, 1, 85) prefers to add just sufficient barium chloride to precipitate the carbonate without affecting the hydroxide. No barium remains in solution, and even if carbon dioxide is absorbed the alkaline carbonate formed remains in solution. The barium chloride is added gradually to the hot solution until precipitation is just complete, and the liquid is filtered into a 250 c.c. flask and an aliquot portion titrated. It is preferable for the liquid containing the precipitate to be diluted to 250 c.c., the precipitate allowed to settle, and 50 c.c. of the supernatant liquid withdrawn. (For various details and precautions, *v.* Sörensen and Andersen, Zeitsch. anal. Chem. 1908, 47, 279.)

Carbonate in presence of hydroxide. The solution is coloured a very faint yellow with phenacetolin, and standard acid is added until the yellow colour changes to a rose tint. The volume of acid required gives the amount of hydroxide present. A further quantity of acid is now added, and the red colour increases in intensity, but eventually changes to yellowish-red, and finally to golden-yellow. At this point a second reading is taken, and the difference between this and the first reading gives the volume of acid corresponding with the carbonate present (Lunge, J. Soc. Chem. Ind. 1882, 1, 56). This method is not available for the estimation of small quantities of hydroxide in presence of large quantities of carbonate (Thomson).

The following method, due to Warder, gives fairly satisfactory results: To the cold dilute solution phenolphthaleïn is added and standard hydrochloric acid run in slowly, the burette tip being immersed in the liquid, till decolourisation takes place. This occurs when all the hydroxide and *half* the carbonate have been neutralised. Methyl orange is then added and the solution titrated again till an acid reaction is indicated. If this second titration requires y c.c. and the first one x c.c., then the carbonate is equivalent to $2y$ c.c. and the hydroxide to $x-y$ c.c. (Küster, Zeitsch. anorg. Chem. 1896, 13, 127; Lunge, Zeitsch. angew. Chem. 1897, 10, 41; North and Lee, J. Soc. Chem. Ind. 1902, 21, 322; *cf.* Cameron, Amer. Chem. J. 1900, 23, 471).

In order to estimate the proportion of carbonate in quick-lime or slaked lime, the purpose for which phenacetolin was originally recommended by Degener, 100–150 grams of the lime are made into a cream with water and diluted to 500 c.c. After vigorous agitation 100 c.c. are withdrawn and diluted to 1000 c.c., and 25 c.c. of this liquid are taken, mixed with phenacetolin, and standard acid added until a pale-rose tint is obtained. In order to estimate both hydroxide and carbonate, the substance is dissolved in standard acid and the excess of acid determined by reverse titration in the usual way (Lunge, *l.c.*).

Acid carbonate in presence of normal carbonate. The *cold and dilute* solution of normal carbonate and acid carbonate is mixed with phenolphthaleïn, and standard acid added, the

burette tip dipping into the liquid to prevent escape of carbon dioxide, until the liquid becomes colourless. At this point, which corresponds with the complete conversion of the normal carbonate into acid carbonate, the volume of acid added is read off. The liquid is then boiled and acid is added gradually until the solution remains colourless even after long boiling, and the volume of acid is again read off. If x represents the first reading, and y the second reading, then $2x$ = the normal carbonate, and $y-2x$ = the acid carbonate (Warder, Chem. News, 1881, 43, 228).

Lunge (J. Soc. Chem. Ind. 1882, 1, 57) proposes a different method based on the reaction:

$$xM_2CO_3 + yMHCO_3 + zNH_3 + (x+y)BaCl_2 = (2x+y)MCl + yNH_4Cl + (x+y)BaCO_3 + (z-y)NH_3.$$

The solution to be tested is mixed with a measured excess of standard (half-normal) ammonia, excess of barium chloride added, and the liquid diluted with recently boiled water to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn and titrated with standard acid in order to ascertain the excess of ammonia. The difference between the volume of ammonia added and that remaining after precipitation gives the volume corresponding with the quantity of acid carbonate in the liquid analysed.

By adding a definite excess of pure sodium hydroxide free from carbon dioxide, a mixture of normal carbonate and hydroxide is obtained which may be analysed as described above.

Ammonia. In order to determine the quantity of free ammonia in a solution of the gas, an accurately measured quantity (10 c.c.) of the liquid is transferred to a light tared flask, and weighed. This gives at once the weight taken for analysis and the sp.gr. The liquid is then titrated with standard acid in the usual way, using litmus, lacmoid, or methyl orange as indicator.

Ammonia in combination is determined by boiling the substance with sodium hydroxide, leading the ammonia into a measured excess of standard acid, and determining the residual acid with standard alkali. The substance is weighed into a flask fitted with a cork, through one hole in which passes a pipette containing a strong solution of sodium hydroxide, whilst through another passes a tube leading to a flask or bulb U-tube containing a known volume of standard acid. The flask or U-tube is fitted with a cork which carries a calcium chloride tube containing beads moistened with some of the acid in order to ensure complete absorption of the ammonia. After addition of the sodium hydroxide solution the liquid is gently boiled for half an hour, and the residual acid determined. From the volume of acid which has combined with the ammonia the quantity of the latter is readily calculated. The sodium hydroxide may be replaced by milk of lime, and the most effectual method of removing the ammonia is to distil the mixture in steam. The use of magnesia in place of sodium hydroxide is not advantageous (Kober, J. Amer. Chem. Soc. 1908, 30, 1279). (For a different method of distilling off the ammonia, *v.* Kober (J. Amer. Chem. Soc. 1908, 30, 1131). *See* also Ronchèse (J. Pharm. Chim. 1907, 25, 611) and Wilkie (J. Soc. Chem. Ind. 1910, 29, 6) for a method of estimation entirely different in principle from the foregoing.)

Hydrochloric, Hydrobromic, Hydriodic, Sulphuric, and **Nitric acids** are readily estimated by direct titration with standard alkali, using methyl orange as indicator.

Oxalic, Tartaric, Citric, Acetic, and **Lactic acids** can likewise be titrated accurately with standard alkali if phenolphthaleïn is used as the indicator (Thomson, *l.c.*). Oxalic acid may also be titrated, using litmus as indicator.

Boric acid gives no very definite reaction with the majority of indicators, but it is quite neutral to methyl orange, and hence the quantity of alkali in akaline borates can be accurately estimated by direct titration with standard acid if methyl orange is used as indicator (Thomson).

The titration of boric acid itself becomes possible if the solution contains at least 30 p.c. of its volume of glycerol. The boric acid then behaves towards phenolphthaleïn as a monobasic acid (Thomson, J. Soc. Chem. Ind. 1893, 12, 432; Jorgensen, Zeitsch. angew. Chem. 1897, 10, 5; Hönig and Spitz, *ibid.* 1896, 9, 549; Copaux, Compt. rend. 1898, 127, 756). A similar result is effected by saturating the solution with mannitol. Since phenolphthaleïn is employed, carbon dioxide must not be present in the solutions to be titrated (Jones, Amer. J. Sci. 1898, 7, 147; Stock, Compt. rend. 1900, 130, 516).

Sulphurous acid can be titrated directly if methyl orange, phenolphthaleïn, or aurin is used as indicator (Lunge, Dingl. poly. J. 250, 530). With methyl orange the hydrogen sulphite $MHSO_3$ is the neutral salt, whilst with the other two indicators the normal salt is neutral. This difference can be utilised for the determination of the relative proportions of normal and acid sulphite in the same solution (Blarez, Compt. rend. 1886, 103, 69; Chem. Soc. Abst. 1886, 50, 918). Caustic soda or potash must be used, since ammonia gives inaccurate results.

Phosphoric and **Arsenic acids** are monobasic with methyl orange, and dibasic with phenolphthaleïn (Joly, Compt. rend. 1882, 94, 529; Chem. Soc. Abst. 1882, 42,692). These acids can be most accurately titrated with barium hydroxide, using phenolphthaleïn as indicator. Towards the close of the reaction, time must be allowed for the gelatinous tribarium phosphate to change into the crystalline dibarium salt (Joly, Compt. rend. 1886, 102, 316; Chem. Soc. Abst. 1886, 50, 418). Advantage can be taken of the different basicity with methyl orange and phenolphthaleïn to estimate phosphoric acid in presence of monobasic acids such as hydrochloric acid (Joly, Compt. rend. 1885, 100, 55; Chem. Soc. Abst. 1885, 48, 348).

(For another simple and accurate method, *v.* Segalle, Zeitsch. anal. Chem. 1895, 34, 33.)

Carbonic acid in solution is estimated by adding excess of ammonia and calcium chloride. The liquid is then boiled, and the precipitated calcium carbonate collected, well washed, and dissolved in a measured excess of standard hydrochloric acid, the excess of acid being determined by means of standard alkali. The volume of normal acid actually used multiplied by 0·022 gives the quantity of carbon dioxide.

Insoluble carbonates are weighed into a flask fitted with a cork which carries a bulb and

delivery tube. The bulb contains moderately strong hydrochloric acid, which is allowed to drop slowly on the carbonate, and the evolved gas is led into a flask containing strong ammonia solution. This flask is closed with a cork, through which passes the delivery tube, which ends just above the surface of the liquid. The cork also carries an exit tube filled with glass beads moistened with ammonia to arrest the last traces of carbon dioxide. When all the gas has been expelled from the carbonate the ammonia is mixed with calcium chloride, boiled, and the precipitate treated as above; *cf.* Gooch and Phelps (Amer. J. Sci. 1895, 50, 101). With slight modification this process can be adapted to the estimation of carbon dioxide in aërated waters.

For the direct titration of carbon dioxide in solution, *v.* Seyler (Analyst, 1897, 22, 312); Ellms and Beneker (J. Amer. Chem. Soc. 1901, 23, 405); and Forbes and Pratt (J. Amer. Chem. Soc. 1903, 25, 742).

Hydrofluoric acid may be accurately titrated with sodium hydroxide free from carbonate, using phenolphthaleïn as indicator (Winkler, Zeitsch. angew. Chem. 1902, 15, 33; *cf.* Haga and Osaka, Chem. Soc. Trans. 1895, 67, 251; and J. Amer. Chem. Soc. 1896, 18, 415; Monatsh. 1897, 18, 749).

Hydrofluosilicic acid may be titrated with sodium or barium hydroxide in the presence of alcohol (an equal volume is added) using phenolphthaleïn or lacmoid as indicator; the alcohol renders the salt produced insoluble in the solution; *v.* Sahlbom and Hinrichsen (Ber. 1906, 39, 2609); *cf.* Schucht and Moller (Ber. 1906, 39, 3693); and Honig and Szabadka (Chem. Zeit. 1907, 31, 1207).

Combined acids in salts may be estimated with approximate accuracy by adding to a solution of the salt a measured excess of sodium hydroxide or carbonate. The liquid is boiled, allowed to cool, and diluted to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn, and the excess of alkali determined by titration. From the volume of alkali used the proportion of acid in the salt is calculated. In order to avoid the error due to the presence of the precipitate, the liquid may be filtered before diluting to a definite volume, but methyl orange or cochineal must be used as indicator in order to avoid any error from carbon dioxide absorbed from the atmosphere. Salts of copper, silver, mercury, cobalt, nickel, iron, and chromium are precipitated with sodium hydroxide; salts of calcium, barium, strontium, magnesium, aluminium, zinc, bismuth, and manganese, with sodium carbonate.

Kieffer's method is useful for coloured solutions, or in presence of normal salts with acid reactions (Annalen, 1855, 93, 386). Sixty grams of crystallised cupric sulphate are dissolved in water, mixed with ammonia until the precipitate is almost but not quite dissolved, diluted to about 900 c.c., the solution left for some time, and the clear liquid siphoned off, or filtered through glass-wool, and diluted to 1000 c.c. If any further precipitate forms, it must be siphoned off or collected. If the solution of cuprammonium sulphate thus obtained is added to an acid liquid, so long as the acid is in excess an ammonium salt and cupric sulphate are formed, but as soon as the free acid is neutralised, the ammonia in a fresh quantity of cuprammonium sulphate reacts on the cupric sulphate already in the liquid and produces a precipitate of a basic salt, the formation of which indicates the point of saturation. The precipitate is most readily seen against a black background. In order to standardise the liquid, 10 c.c. of normal sulphuric acid are placed in a flask or beaker and Kieffer's solution added until a permanent precipitate is produced, and from the volume of solution required, its strength in terms of normal acid is readily calculated. The strength of the solution gradually diminishes, and it must be titrated from time to time. In making an actual determination, the Kieffer's solution is added to the liquid to be tested until a permanent precipitate is formed. The method is not very accurate, owing mainly to the fact that the precipitate is not quite insoluble in solutions of ammonium salts, and therefore the end reaction does not take place until the liquid is saturated with the basic salt. The magnitude of the error depends on the concentration of the solution. When the liquids to be titrated contain barium, strontium, &c., the Kieffer's solution must be prepared with cupric nitrate.

(For other methods, *v.* Sims (Chem. News, 1907, 95, 253) and Ahlum (Chem. Soc. Proc. 1906, 22, 63).)

Bibliography.—Mohr's Chemisch-Analytische Titrirmethode, 6th ed. 1886; Sutton's Volumetric Analysis, 9th ed. 1904; Fresenius' Quantitative Chemische Analyse, v. 2, 6th ed.; Treadwell-Hall, Analytical Chemistry, v. 2, 2nd ed. 1910; Lunge's Technical Chemist's Handbook; Cohn's Indicators and Test Papers, 2nd ed. 1902; Glaser's Indikatoren der Acidimetrie und Alkalimetrie, 1901. G. T. M.

ACID ALIZARIN, -BLACK, -BROWNS, -PONCEAU, -YELLOWS *v.* AZO- COLOURING MATTERS.

ACID MAGENTA *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACID VIOLET *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACIDINE BRILLIANT RED *v.* AZO- COLOURING MATTERS.

ACME YELLOW *v.* AZO- COLOURING MATTERS.

ACOKANTHERA SCHIMPERI. The arrow-poisons of East Africa are prepared from the wood of the genus *Acokanthera*, which contains a crystalline glucoside, *acokantherinin* $C_{30}H_{46}O_{12}$, H_2O (Arnaud), $C_{34}H_{50}O_{12}$ (Faust). Crystallises from water and alcohol; insol. in ether or chloroform: sol. neutral and bitter. Strong sulphuric acid gives a red colour eventually becoming green. On boiling with dilute mineral acids is hydrolysed with formation of rhamnose. Is optically inactive, softens at 130° and decomposes at 220°. The pharmacological action of the glucoside resembles that of members of the digitalin group (Fraser and Tillie, Proc. Roy. Soc. 58, 70; Faust, Chem. Zentr. 1902, 2, [19] 1217).

ACONINE, ACONITE, ACONITINE, ACONITIC ACID *v.* VEGETO-ALKALOIDS.

ACORUS CALAMUS (Linn.). The common sweet flag. The root is used by distillers to flavour gin, and the essential oil by snuff-makers for scenting snuff. It contains a glucoside

termed *acorin* $C_{36}H_{60}O_6$ (Faust, Bull. Soc. chim. [2] 9, 392; Thoms, Arch. Pharm. [3] 24, 465) (*v.* CALAMUS).

ACRIDINE $C_{13}H_9N$. Crude anthracene contains basic substances, and among them acridine, which can be isolated by extracting it with dilute sulphuric acid and adding potassium dichromate to the acid solution. The precipitated acridine chromate is then recrystallised from water, treated with ammonia, and the base crystallised from hot water (Graebe and Caro, Annalen, 158, 265; Ber. 13, 99).

Acridine has also been obtained synthetically by passing the vapours of orthotolylaniline and of orthoditolylamine through a tube heated to dull redness (G., Ber. 17, 1370); by severally heating formic acid and diphenylamine (Bernthsen and Bender, Ber. 16, 767, 1802), chloroform, diphenylamine and zinc oxide (Fischer and Körner, Ber. 17, 101), and aniline and salicylaldehyde (Möhlau, Ber. 19, 2451) with zinc chloride; by passing *o*-amidodiphenyl methane through a layer of lead oxide heated to dull redness (Fischer and Schütte, Ber. 26, 3085). By distilling tetrahydroacridine with litharge (Borsche, Ber. 41, 2203), and also from acridone (Decker and Dunant, Ber. 39, 2720; Ullmann, Bader and Labhardt, Ber. 40, 4795).

Properties.—Acridine crystallises in small colourless needles, or four-sided rhombic prisms, sublimes at 100°, melts at 111°, boils above 360° without decomposition, and distils with steam. It is sparingly soluble in hot water, but readily soluble in alcohol, ether, or carbon disulphide, yielding solutions showing a blue fluorescence. When inhaled either as dust or vapour it causes violent sneezing, and in solution both it and its salts cause much irritation on the skin. On treatment with nitric acid it yields two nitroderivatives (m.p. 154° and 214°) and a dinitroderivative (G. and C.); potassium permanganate oxidises it to 2 : 3-quinolinedicarboxylic acid $C_9H_5N(CO_2H)_2$, and sodium amalgam reduces it to *hydroacridine* $C_{13}H_{11}N$ (B. and B., Ber. 16, 1971; G., Ber. 16, 2831). The salts are yellow and crystallise well, but are decomposed into their constituents on boiling. Heated with hydrogen and finely divided nickel, it forms 2 : 3-dimethyl quinoline (Padoa and Fabris, Atti R. Acad. Lincei, 1907, [v.] 16, i. 921). The halogen addition compounds of acridine and its derivatives are formed by the direct action of the halogen on the acridine (Senier and Austin, Chem. Soc. Trans. 1904, 1196); or by the action of a mixture of phosphorus oxychloride and pentachloride on thioacridone (Edinger, Ber. 33, 3770; D. R. P. 120586; Edinger and Arnold, J. pr. Chem. [ii.] 64, 182, 471; D. R. P. 122607); for other methods, compare Dunstan and Stubbs (Ber. 39, 2402; D. R. P. 126795), Graebe and Lagodzinski (Annalen, 276, 48). Alkyl iodomagnesium compounds of acridine have also been obtained (Senier, Austin, and Clarke, Chem. Soc. Trans. 1905, 1469). When exposed to sunlight acridine forms pale-yellow crystals, m.p. 276° (Orndorff and Cameron, Amer. Chem. J. 1895, 17, 658).

2 : 7-**dimethyl- 3 : 6-diaminoacridine** or *acridine yellow* $NH_2{\cdot}C_6H_2Me\langle{}^{CH}_{N}\rangle C_6H_2Me{\cdot}NH_2$ is obtained by heating under pressure tetraminoditolylmethane with hydrochloric acid and water, the product is then oxidised with ferric chloride or potassium percarbonate $K_2C_2O_6$ or hydrogen peroxide, and the resulting metallic salt decomposed with hydrochloric acid (D. R. P. 52324; Lymn, J. Soc. Chem. Ind. 1897, 16, 406; Ullmann and Marić, Ber. 34, 4308; Haase, Ber. 36, 589). It forms yellow crystals melting above 300°, soluble in alcohol, acetone and pyridin, and forming a yellow solution in sulphuric acid with a green fluorescence. It yields derivatives which form yellow, orange, brownish-, greenish-, and reddish-yellow dyes, and can be used on cotton, leather, wool, and silk. The following are some of the methods of preparation: (1) heating with mineral acids under pressure, when it yields aminohydroxy- and dihydroxydimethyl acridine (D. R. P. 121686; Chem. Zentr. 1901, ii. 78; J. Soc. Chem. Ind. 21, 37); (2) heating with monochloracetic acid and water under pressure (D. R. P. 133788; Chem. Zentr. 1902, ii. 616; D. R. P. 136729; Chem. Zentr. 1902, ii. 1396); (3) heating with formaldehyde and mineral acids under pressure (D. R. P. 135771; Chem. Zentr. 1902, ii. 1233; J. Soc. Chem. Ind. 21, 112, 544, 402); (4) by treatment with formaldehyde and aromatic bases (J. Soc. Chem. Ind. 22, 140; D. R. PP. 131365, 132116; Chem. Zentr. 1902, ii. 172; i. 1288); (5) heating with benzyl chloride in presence of nitrobenzene (J. Soc. Chem. Ind. 21, 701, 1530); (6) treating with aqueous formic acid (*ibid.* 21, 90); (7) heating with glycerol at 150°–180° (D. R. P. 151206); (8) alkylation (Ullmann and Marić, *l.c.*; D. R. P. 79703; J. Soc. Chem. Ind. 19, 1010; 24, 840).

Phenylacridine $C_{19}H_{13}N$ is obtained by heating diphenylamine with benzoic acid and zinc chloride at 260° (Bernthsen, Ber. 15, 3012; 16, 767, 1810), and melts at 181°. The *hydroxyphenylacridines* which form yellow dyes in mineral acids can be obtained similarly by using the corresponding hydroxy acid (Landauer, Bull. Soc. chim. 31, 1083).

Other acridine dyes can be obtained by heating tetraminoditolylmethane or the leuco-compounds of amino-acridines with mineral acid and alcohol under pressure, the shade depending on the quantity and nature of alcohol and of acid used (J. Soc. Chem. Ind. 20, 888; 22, 1126; 23, 932). Also by the interaction of an aromatic or aliphatic *m*-diamine with an aldehyde (*ibid.* 21, 1529; Chem. Zeit. 14, 334; J. Soc. Chem. Ind. 17, 573; 22, 1241). By heating the formyl derivatives of *m*-diamines with ammonia salts or salts of organic bases at 150°–200° (D. R. PP. 149409, 149410). For other methods of preparing acridine derivatives, many of which have dyeing properties, compare: Bizzarri, Gazz. chim. ital. 20, 407; Decker, J. pr. Chem. 153, 161; Mohlau and Fritzsche, Ber. 26, 1034; Volpi, Gazz. chim. ital. 21, ii. 228; J. Soc. Chem. Ind. 19, 732; 21, 338, 701, 911, 1528; Goodwin and Senier, Chem. Soc. Trans. 1902, 285; J. Soc. Chem. Ind. 22, 23, 90; D. R. PP. 133709, 107517; Ullmann, Ber. 36, 1017, 1025; D. R. P. 141297, 141356; Bünzley and Decker, Ber. 37, 575; Fox and Hewitt, Chem. Soc. Trans. 1904, 529; 1905, 1058; Schöpff, Ber. 26, 1121; Ber. 27, 2316; Duval, Compt. rend. 142, 341; Koenigs, Ber. 32, 3599; Ullmann and Maag, Ber. 40, 2515; Austin, Chem. Soc. Trans. 1908, 1760; D. R. PP. 118075,

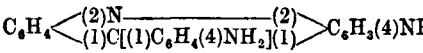
152662; Pope and Howard, Chem. Soc. Trans. 97, 83.

Naphthacridine and its derivatives, which can also be used as dyes, have been prepared (J. Soc. Chem. Ind. 18, 826; 19, 237; Ullmann and Naef, Ber. 33, 905, 912, 2470; J. Soc. Chem. Ind. 20, 37, 573; D. R. P. 126444; Ullmann and Baezner, Ber. 35, 2670; 37, 3077; Ullmann and Felzvadjian, *ibid.* 36, 1027; Ullmann and Farre, *ibid.* 37, 2922; Ullmann and Fitzenham, *ibid.* 38, 3787; Baezner and Gardiol, *ibid.* 39, 2623; Baezner, *ibid.* 2650; Senier and Austin, Chem. Soc. Trans. 1907, 1233, 1240; Senier and Compton, *ibid.* 1907, 1927; Baezner and Gueorgnieff, Ber. 39, 2438).

In the case of many of the naphthacridine derivatives, patents have been taken by Ullmann (D. R. PP. 104667, 104748, 108273, 117472, 119573, 123260, 127586, 128754, 130721, 130943); the further alkylation of some of these, as well as of other acridine compounds has been patented by the A.-G. für Anilin-Fabrikation (D. R. PP. 117065, 129479).

ACRIDINE DYESTUFFS. Acridine, though colourless, shows absorption bands in the ultra-violet. The salts are yellow, and the addition products with alkyl halides are also coloured. (For absorption spectra, *see* Dobbie and Tinkler, Chem. Soc. Trans. 1905, 87, 269.) The salts of acridine itself are useless tinctorially, but amino- and alkyl-amino- derivatives of acridine, phenylacridine, &c., are useful dyestuffs, generally producing yellow shades. For the preparation of these substances, synthesis is generally resorted to, although acridine may be nitrated (Graebe and Caro, Annalen, 1871, 158, 275), and α-nitro-acridine has been reduced to an amino-acridine (Anschütz, Ber. 1884, 17,437).

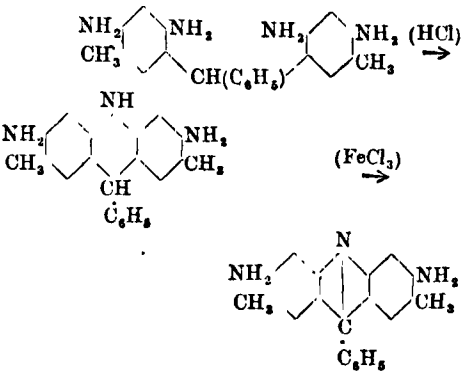
One dyestuff of the acridine series, *chrysaniline*, is formed as a by-product in the manufacture of magenta (Hofmann, Jahresb. 1862, 346). Its constitution



was determined by O. Fischer and G. Körner; probably two molecules of aniline and one of *p*-toluidine condense when oxidised to *opp*-triaminotriphenylmethane, this yielding chrysaniline when further oxidised. This view is supported by the fact that when *opp*-triaminotriphenylmethane is heated with arsenic acid to 150°–180°, chrysaniline is produced (Annalen, 1884, 226, 188).

The processes for preparing amino- derivatives of acridine on a technical scale may be illustrated by the methods of preparing *benzoflavine*, *rheonine*, and *diaminoacridylbenzoic acid*.

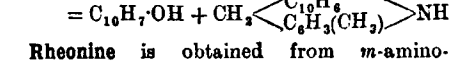
Symmetrical diamino-acridines are obtained by the condensation of aldehydes with *m*-diamines, removal of the elements of ammonia from the resulting tetra-amino- compound by heating with hydrochloric acid, and oxidation of the dihydro-acridine thus produced with ferric chloride. In the case of *benzoflavine* benzaldehyde and *m*-toluylene-diamine are employed.



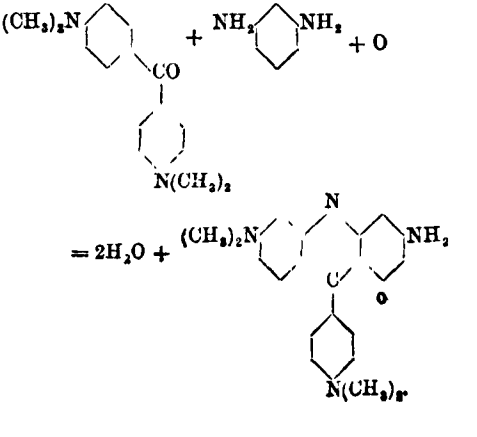
The reaction is capable of considerable modification; thus from formaldehyde and dimethyl-*m*-phenylenediamine, *acridine orange* is produced in an analogous manner. It should be noted, however, that *m*-phenylenediamine gives products which are evidently mixtures, and cannot be purified (R. Meyer and R. Gross, Ber. 1899, 32, 2365).

The reaction between an aldehyde and a *m*-diamine may be carried out in two stages; Meyer and Gross (*l.c.* p. 2358), for example, prepared a monobenzylidene derivative of *m*-toluylenediamine and converted this into tetraminoditolyl-phenylmethane by warming its alcoholic solution with the hydrochloride of *m*-toluylenediamine for three hours at 60°–70°. Acridine itself may be obtained in good yield by heating salicylidene-aniline with phosphorus pentoxide to 250° (Blau, Monatsh. 1897, 18, 123).

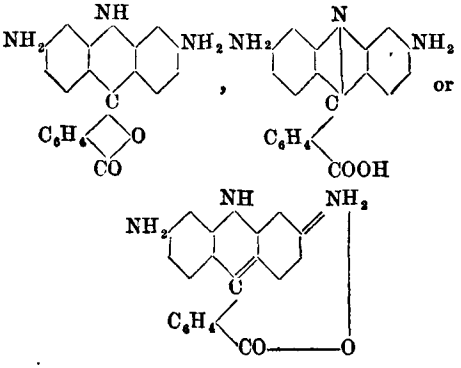
A closely-related synthesis of acridine derivatives is that of F. Ullmann and E. Naef (Ber. 1900, 33, 905). When dihydroxydinaphthylmethane, the product of the interaction of formaldehyde and β-naphthol, is heated with *p*-toluidine hydrochloride, methylhydronapthacridine is produced with elimination of β-naphthol.



Rheonine is obtained from *m*-aminophenylauramine or tetramethyldiaminobenzophenone and *m*-phenylenediamine at 200°, using zinc chloride as condensing agent.



Some derivatives of xanthene, when energetically treated with ammonia, suffer replacement of the pyrone oxygen atom by an imino-group. By the prolonged heating of fluorescein with ammonia under pressure, R. Meyer (Ber. 1888, 21, 3376) obtained an acridine derivative, to which one of the three following constitutions is assignable :—



The salts of the tetra-ethyl derivative of this compound form the dyestuff known as *flaveosine*.

Acridine Orange NO (Farbwerk Mühlheim, D. R. P. 59179, 17 Dec. 1889), $C_{13}H_7N[N(CH_3)_2]_2 \cdot HCl \cdot ZnCl_2$ was discovered by Bender. It is produced by condensation of dimethyl-*m*-phenylenediamine with formaldehyde and proceeding according to the method referred to above. It forms an orange powder which dissolves in water or alcohol with orange-red colour and greenish fluorescence. The aqueous solution is reddened by hydrochloric acid; sodium hydroxide gives a yellow precipitate. The solution in concentrated sulphuric acid is nearly colourless and has a greenish fluorescence, dilution with water produces successively red and orange colouration. The dye gives orange shades, fairly fast to light and soap, on cotton mordanted with tannin; it is also suitable for printing and leather-dyeing.

The analogous dyestuff from diethyl-*m*-phenylenediamine is described in D. R. P. 67609, the substances derived from monoalkyl-phenylenediamines in D. R. P. 70935.

Another method of preparing acridine orange is to heat 12 kilos. of aminodimethylaniline either with 10 kilos. of formic acid (sp.gr. 1·2) and 10 kilos. of zinc chloride gradually to 150°–160°, or with 12 kilos. of dehydrated oxalic acid, 10 kilos. of glycerol and 11 kilos. of zinc chloride to 150°. Heating and stirring are continued as long as any darkening of shade can be observed, ammonia is liberated during the reaction, and formic acid having been employed instead of formaldehyde, the product when worked up yields the dyestuff instead of its leuco-compound (D. R. P. 67126).

The formyl derivatives of *m*-diamines may also be used (D. R. PP. 149049, 161699), or the 'methane' carbon atom may be furnished by various formyl derivatives such as formanilide (D. R. P. 149410).

Acridine Orange, R extra (Farbwerk Mühlheim, D. R. P. 68908, 7 Feb. 1890). The dyestuff is the hydrochloride of tetramethyldiamino-9-phenylacridine, and is obtained from dimethyl-*m*-phenylenediamine and benzaldehyde. Its reactions and uses are similar to those of Mark NO.

D. R. P. 68908 also mentions the use of *m*-aminodimethyl-*o*-toluidine. If the latter base be condensed with *p*-nitrobenzaldehyde to a triphenylmethane derivative, the nitro- group reduced and condensation and oxidation effected in the usual way, an acridine dyestuff possessing two tertiary and one primary amino- group is obtained (D. R. P. 70065; compare D. R. P. 71362).

The use of acetaldehyde as a component was claimed by the Ges. f. Chem. Ind. (D. R. P. 143893, 13 March, 1902).

Acridine Yellow (Farbwerk Mühlheim, D. R. P. 52324, 27 June, 1889) was, like the two preceding colours, discovered by Bender. Its constitution is that of a 3 : 6-diamino-2 : 7-dimethylacridine hydrochloride; it is produced from formaldehyde and *m*-toluylenediamine. It forms a yellow powder soluble in water and alcohol with yellow colour and green fluorescence; yellow precipitates are obtained with hydrochloric acid (hydrochloride) and sodium hydroxide (free base). Silk is dyed a greenish yellow with green fluorescence, cotton (tannin mordant) is coloured yellow.

The salts with aliphatic acids, *e.g.* formate and acetate, are more soluble (Farbenfabriken vorm. F. Bayer, D. R. P. 140848, 13 March, 1903). Acridine yellow is converted into an orange yellow, more easily soluble dyestuff by heating with twice its weight of glycerol for 4–6 hours to 170°–180° (Badische Anilin und Soda-Fabrik, D. R. P. 151206, 26 July, 1903).

(For the action of aldehyde on aniline yellow, *see* D. R. P. 144092.) Compounds, probably of acridinium type, are obtained from aniline yellow by the action of monochloracetic acid (M. L. B., D. R. PP. 133788, 136729, 152662) and other dyestuffs by condensation with formaldehyde and *m*-diamines (D. R. PP. 131365, 132116, 135771). Either one or both of the amino- groups in acridine yellow and analogous dyestuffs are replaced by hydroxyl on heating with dilute sulphuric acid to 180°–220° (D. R. P. 121686), and similar compounds may be obtained from formaldehyde by condensation with amino-cresols (D. R. P. 120466).

Dibenzyl aniline yellow is claimed by Bayer & Co. as a useful leather dye (D. R. P. 141297).

Benzoflavine (several marks), 3 : 6-diamino-2 : 7-dimethyl-9-phenylacridine hydrochloride $C_{13}H_4N(C_6H_5)(NH_2)_2(CH_3)_2.HCl$, was discovered by Rudolph in 1887, and introduced commercially by K. Oehler in 1888 (D. R. PP. 43714, 28 July, 1887; 43720, 45294, 45298). Its preparation has been given above. The dye, which is usually mixed with dextrin, forms an orange powder, difficultly soluble in cold water, more easily in hot. Both aqueous and alcoholic solutions are orange, with strong green fluorescence. Hydrochloric acid gives an orange precipitate, sodium hydroxide liberates the yellowish-white base. The solution in concentrated sulphuric acid is greenish yellow, and shows a very strong green fluorescence. It may be used for dyeing both mordanted and unmordanted cotton. The acetate and lactate are more readily soluble (Bayer, D. R. P. 142453, 19 April, 1902); it behaves like acridine yellow when heated with glycerol.

The **Patent Phosphines** of the Ges. f. Chem. Ind. in Basel are obtained by alkylation of benzoflavine and acridine yellow (D. R. P. 79703; compare D. R. P. 131289).

Coriophosphines (Bayer & Co.). These dyestuffs, which are suitable for leather-dyeing, are probably unsymmetrically alkylated diaminoacridines obtained by condensation of formaldehyde with one molecule of an asymmetrically dialkylated *m*-diamine and one molecule of a non-alkylated or monoalkylated *m*-diamine, with subsequent elimination of ammonia, and oxidation (D. R. P. 133709).

Chrysaniline $C_{19}H_{15}N$ occurs under many other names commercially, *e.g.* Leather yellow, Xanthine, Philadelphia yellow G, Leather brown, Phosphine (several marks), &c. Reference to its occurrence in the manufacture of magenta has already been made. Numerous methods for preparing homologues and analogues of this substance have been patented (D. R. PP. 65985, 78377, 79263, 79585, 79877, 81048, 94951, 102072, 106719, 114261, 116353). The method adopted for this purpose by Meister, Lucius, and Brüning may be mentioned (D. R. P. 65985, 2 April, 1892). *p*-Toluidine and its hydrochloride are heated with ferric chloride (oxygen-carrier), and *m*-nitroaniline gradually added. The resulting dyestuff is the next higher homologue of chrysaniline, containing a methyl- group in position 7.

According to Friedländer (Fortschritte der Theerfarbenfabrikation V. 373), the yields produced by this method are not good, but the reaction between *p*-aminobenzaldehyde or a derivative and phenyl-*m*-phenylene- (or toluylene-) diamine proceeds nearly quantitatively:

$$C_6H_5{\cdot}NH{\cdot}C_7H_6{\cdot}NH_2 + C_6H_4(NH_2)CHO + O = 2H_2O + C_6H_4\begin{cases}N\\ \\ C{\cdot}C_6H_4{\cdot}NH_2\end{cases}\!\!>C_7H_5NH_2$$

B. A. S. F., D. R. PP. 94951, 102072).

Chrysaniline forms an orange-yellow powder, soluble in water and alcohol with reddish-yellow colour and yellowish-green fluorescence. The solution is unaltered by hydrochloric acid; sodium hydroxide gives a bright yellow precipitate. Chrysaniline is chiefly used in leather dyeing.

Corioflavines (Griesheim-Elektron). These dyestuffs, which occur commercially as marks G, GG, R, and RR, are used in leather-dyeing and calico-printing. They form red or reddish-brown powders, which dissolve in concentrated sulphuric acid with yellow or orange colouration and green fluorescence; these solutions turn red or reddish-brown on dilution.

Flaveosine (Meister, Lucius, and Brüning, D. R. P. 49850, 11 May, 1889) is a tetraethyldiaminoacridylbenzoic acid, which is obtained by heating *m*-acetaminodimethylaniline with phthalic anhydride. It has been examined by Grandmougin and Lang (Ber. 1909, 42, 4014).

The hydrochloride crystallises in shining brownish-yellow needles, the sulphate in prisms exhibiting a cantharides lustre. The base is precipitated from the salts by sodium carbonate, and forms golden-yellow shining leaflets.

Flaveosine dyes silk golden yellow (yellowish-green fluorescence) from a feebly acid bath; wool and cotton (tannin mordant) are coloured reddish yellow. The colours are fast.

Substances closely related to flaveosine are obtained by the esterification of the product of the interaction of ammonia and fluorescein (B. A. S. F., D. R. PP. 73334, 75933; compare D. R. P. 141356).

Rheonine (Badische Anilin und Soda-Fabrik). This dyestuff was discovered by C. L. Müller (D. R. P. 82989, 16 Dec. 1894). Its method of preparation has already been given. Rheonine forms a brown powder, soluble in water and alcohol, with brownish-yellow colour and green fluorescence. Hydrochloric acid turns the solution brownish-red, caustic soda gives a bright brown precipitate. It is used for obtaining brownish-yellow shades on leather or cotton (tannin). Two marks, N (brighter) and A (darker), are in use.

The use of diaminobenzophenone and of Michler's hydrol for condensation with *m*-diamines have been patented (M. L. B., D. R. P. 89660 and B. A. S. F., D. R. P. 85199 respectively).

Many acridine and naphthacridine dyestuffs containing only one amino- group have been described (D. R. PP. 104667, 107517, 107626, 108273, 118075, 118076, 125697, 130360); and it has also been observed that dyestuffs can be obtained when only one molecular proportion of a *m*-diamine is used with formaldehyde (D. R. P. 136617). J. T. H.

ACRODEXTRINS *v.* DEXTRINS.

ACROSE *v.* CARBOHYDRATES.

ACTINIUM. A radioactive element, discovered by Debierne in the precipitate produced by adding ammonia and ammonium sulphide to the filtrate from the hydrogen sulphide precipitate obtained in the course of analysing pitchblende (Debierne, Compt. rend. 129, 593; 130, 906). In fractionating the rare earths thus obtained from pitchblende by means of their double nitrates with magnesium nitrate, actinium accumulates in the more soluble portions together with neodymium and samarium (Compt. rend. 139, 538). The predominating rare earth in pitchblende is thorium; but actinium also occurs in uranium minerals containing no thorium (Szilárd, Chem. Soc. Abstr. 1909, ii. 663).

Actinium has not been obtained pure, but it appears to resemble thorium chemically (*cf.* however, Giesel, Ber. 40, 3011). It is precipitated by oxalic acid, hydrofluoric acid, and by ammonia. Actinium preparations are highly radioactive, imparting induced radioactivity to surrounding objects (Curie and Debierne, Compt. rend. 132, 548), and, like radium, they spontaneously give rise to helium (Debierne, Compt. rend. 141, 383); they are not luminescent. Their aqueous solutions slowly evolve hydrogen and oxygen in the proportions necessary to form water. Actinium salts also evolve an *emanation*, an inert gas having a molecular weight of approximately 70, according to diffusion experiments (Debierne, Compt. rend. 136, 446, 767; 138, 411; Bruhat, Comp. rend. 148, 628; Russ, Phil. Mag. 17, (vi.) 412), and condensing to a liquid at $-120°$ to $-150°$ (Kinoshita, Phil. Mag. 16, (vi.) 121).

The spontaneous decomposition of actinium appears to give rise to six successive products: *radio actinium* (Hahn, Ber. 39, 1605; Phil. Mag. 13, (vi) 165), which is said to resemble the

alkaline earths (Giesel, Ber. 40, 3011), and which changes into *actinium X*, a substance soluble in ammonia; this transforms into *actinium emanation*, from which *actinium A*, *actinium B*, and *actinium C* successively arise (Hahn and Meitner, Chem. Soc. Abstr. 1908, ii. 920); they are induced active deposits. Actinium itself is rayless; all the other products except actinium A emit α-particles; and radio actinium, actinium A, and actinium C emit β-rays (Hahn and Meitner, Chem. Soc. Abstr. 1908, ii. 1007).

Actinium is identical with the substance *emanium* discovered by Giesel (*v.* Giesel, Ber. 35, 3608; 36, 342; 37, 1696, 3963; Debierne, Comp. rend. 139, 538; Hahn and Sackur, Ber. 38, 1943; *cf.* Marckwald, Ber. 38, 2264).

ADAMANTINE SPAR *v.* CORUNDUM.

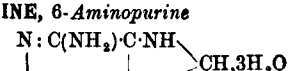
ADAMITE. An artificial abrasive made in Austria.

ADAMITE. Hydrated basic zinc arsenate, $Zn_3(AsO_4)_2{\cdot}Zn(OH)_2$, crystallising in the orthorhombic system. First found in 1866 as violet crystals in a silver-mine at Chañarcillo, Chile, and subsequently as greenish and yellowish crystals in considerable abundance in the zinc-mines at Cape Garonne in France, and Laurion in Greece.

ADANSONIA DIGITATA (Linn.), the *Baobab tree*, yields a fibre which has been used in paper-making. Its bark (Gowik Chentz or Churee Chentz) is said by Duchaissaing to be a useful substitute for cinchona (Dymock, Pharm. J. [3] 7, 3).

ADENASE *v.* ENZYMES.

ADENINE, 6-*Aminopurine*



discovered in the pancreatic gland and spleen of the ox, occurs in all vegetable and animal tissues rich in cells (Kossel, Ber. 1885, 18, 79, 1928; Zeitsch. physiol. Chem. 1886, 10, 248); thus it has been extracted from tea leaves (Kossel, *l.c.*), from beet-juice (*v.* Lippmann, Ber. 1896, 29, 2645),from the young shoots of bamboo (Totani, Zeitsch. physiol. Chem. 1909, 62, 113); from human excretory products (Krüger and Schittenhelm, Zeitsch. Physiol. Chem. 1902, 35, 159), and from herring brine (Isaac, Chem. Zentr. 1904, ii. 647; from Beitr. chem. physiol. Path. 1904, 5, 500); it is probably one of the degradation products of nucleïn (Schindler, Zeitsch. physiol. Chem. 1889, 13, 432), and is found in small quantity when nucleïn is heated with dilute sulphuric acid (Kossel, Ber. 1885, 18, 1928).

Adenine is isolated from tea extract after the removal of caffeine by precipitating the cuprous compound $C_5H_3N_5Cu_2$ by means of copper sulphate and sodium bisulphite, and decomposing the precipitate with ammonium sulphide; the crude adenine is then isolated from the filtrate in the form of the sulphate. For the method of separating adenine from other purine bases compare Schindler, Zeitsch. physiol. Chem. 1889, 13, 432). The synthesis of adenine has been effected by reducing with hydriodic acid 2-amino-2 : 8-dichloropurine obtained by the action of aqueous ammonia on trichloropurine (E. Fischer, Ber. 1897, 30, 2226; 1898, 31, 104; Böhringer and Sons, D. R. P. 96927, 24/3, 97; Traube, Annalen, 1904, 331, 64).

Adenine crystallises from dilute aqueous solution in long rhombic needles that become anhydrous at 110°, and melt with decomposition when rapidly heated at 360°–365° (Fischer, *l.c.*), and sublime in microscopic needles without decomposition at 220°. Adenine is sparingly soluble in cold (1 : 1086) and readily soluble in hot water (1 : 40); insoluble in ether or chloroform, sparingly so in alcohol. It forms compounds with bases, acids, and salts. The *nitrate* $C_5H_5N_5,HNO_3,\frac{1}{2}H_2O$ is crystalline, and the dry salt dissolves in 110·6 parts of water; the *hydrochloride* $C_5H_5N_5,HCl,\frac{1}{2}H_2O$ forms transparent monoclinic prisms $a:b:c=2{\cdot}0794:1:1{\cdot}8127$, $\beta = 61°\ 40'$ the anhydrous salt dissolves in 41·9 parts of water; the *chloracetate* $C_5H_5N_5$, $C_2H_3O_2Cl$ melts and decomposes at 162°–163°; the *sulphate* $(C_5H_5N_5)_3,H_2SO_4,2H_2O$, the *oxalate* $C_5H_5N_5,C_2H_2O_4,H_2O$, and *dichromate* $(C_5H_5N_5)_2$, $H_2Cr_2O_7$ are crystalline; the *picrate* $C_5H_5N_5$, $C_6H_3N_3O_7$ is stable at 220°, and is so sparingly soluble in cold water (1 : 3500) that it is used as a means of estimating adenine in solution (Ber. 1890, 23, 225); the *picrolonate* $C_5H_5N_5$, $C_{10}H_8O_5N_4$ crystallises from water and melts at 265° (Levene, Biochem. Zeitsch. 1907, 4, 320). The *platinichloride* $(C_5H_5N_5)_2,H_2PtCl_6$ crystallises from dilute solution in needles, and yields the *salt* $C_5H_5N_5,HCl,PtCl_4$ when a concentrated solution is boiled. The *acetyl* derivative $C_5H_4N_5Ac$ does not melt at 260°, the *benzoyl* derivative $C_5H_4N_5Bz$ has m.p. 234°–235° (Kossel, Ber. 1886, 20, 3356). The *methyl* and *benzyl* derivatives have been prepared (Thoiss, Zeitsch. physiol. Chem. 13, 395). *Bromadenine* $C_5H_4N_5Br$ is strongly basic, forms an insoluble *picrate*, and on oxidation with hydrochloric acid and potassium chlorate yields alloxan, urea, and oxalic acid (Bruhns, Ber. 1890, 23, 225; Krüger, Zeitsch. physiol. Chem. 1892, 16, 329). Adenine is converted into hypoxanthine by the action of nitrous acid (Kossel, Ber. 1885, 18, 1928).

M. A. W.

ADHESIVES, as distinguished from cements, may be defined to be substances or preparations of a gummy or gelatinous character used for the purpose of joining together or effecting the mutual adhesion of the surfaces of bodies. They are usually substances which (1) soften in water, *e.g.* gum arabic, isinglass, glue, &c.; (2) gelatinise in water or other menstruum, and harden either by the evaporation of the solvent or its absorption by the cohering surfaces, *e.g.* liquid glue, gelatine dissolved in acetic acid, rubber or guttapercha in benzene, &c.; or (3) which soften on heating and congeal on cooling, *e.g.* marine glue, shellac, &c. The surfaces of the articles to be joined should be perfectly clean; they should be brought into intimate contact, and as little of the adhesive as possible employed. In certain cases perfect contact is ensured by heating the parts to be joined to a temperature such that the adhesive solidifies only when union is effected.

Solutions of gum arabic, or of dextrin, or British gum, mixed with acetic acid, are frequently employed in the case of paper. Flour or starch mixed with water containing a little alum so as to form a thick cream, which is then heated to boiling, and when cold mixed

with oil of cloves, thymol, phenol, or salicylic acid so as to preserve it, makes an effective adhesive. A transparent paste may be made by the use of rice starch instead of ordinary flour. Occasionally a small quantity of linseed oil or glycerol is added in the case of labels exposed to moisture. Or the labels may be protected from damp by being coated with a mixture of 2 pts. shellac, 1 pt. borax dissolved in 16 pts. of boiling water. An alternative method is to apply a coating of copal varnish.

A strong adhesive may be made from shredded gelatine, swollen in water containing 25 p.c. of glacial acetic acid and applied hot. The mixture should be kept in a closely corked phial. Another recipe: Dissolve 60 pts. borax in 420 pts. water, add 480 pts. dextrin and 50 pts. glucose, and heat carefully—not above 90°—with constant stirring until the whole is in solution; replace the evaporated water and filter through flannel (Hiscox).

Wheat flour rich in proteins is mixed with concentrated sulphite liquors and evaporated to a suitable consistency (Robeson). Dry casein mixed with half its weight of borax and a sufficiency of water makes an excellent adhesive for broken china or earthenware. Milk casein dissolved in alkali and an alkaline silicate, such as water-glass, and mixed with a solution of magnesium or calcium chloride, also constitutes an effective adhesive.

Metallic surfaces after having been rubbed with an alcoholic solution of hydrochloric acid may be caused to adhere by means of a mixture of 10 pts. tragacanth mucilage, 10 pts. honey, and 1 pt. flour (Spon).

A *marine glue* may be made by dissolving 10 pts. caoutchouc in 120 pts. benzene, and adding the solution to 20 pts. melted asphaltum, the mixture being poured into moulds to consolidate. In order to use it the glue is soaked in boiling water and heated over a flame until liquid.

ADIPIC ACID. *Butane-α-δ-dicarboxylic acid* $CO_2H{\cdot}(CH_2)_4{\cdot}CO_2H$. Obtained by the action of nitric acid on sebacic acid, or on tallow, suet, and other fatty bodies (Arppe, Z. 1865, 300; Laurent, Ann. Chim. Phys. [2] 66, 166; Bromeis, Annalen, 35, 105; Malaguti, Ber. 1879, 572). It is present in beet-juice (Lippmann, Ber. 1891, 3299), and may be obtained from Russian petroleum by distilling the fraction containing naphthalene hydrocarbons (Aschan, Ber. 1899, 1769). It may be prepared by the reduction of mucic acid (Crum-Brown, Annalen, 125, 19), saccharic acid (de la Motte, Ber. 1879, 1572), *iso*saccharic acid with hydriodic acid and phosphorus, or of muconic acid with sodium amalgam (Marquardt, Ber. 1869, 385); by heating β-iodopropionic acid with silver (Wislicenus, Annalen, 149, 221); by the electrolysis of the potassium salt of the monoethyl ester of succinic acid, whereby the diethyl ester of adipic acid is produced (Brown and Walker, Annalen, 261, 117); by oxidising cyclo-hexanone with potassium permanganate in the presence of sodium carbonate (Rosenlew, Ber. 1906, 2202; Mannich and Hancu, Ber. 1908, 575).

Adipic acid crystallises in monoclinic laminæ, melts at 149°, and sublimes at a still higher temperature (Wirz, Annalen, 104, 257). *Cyclo*pentanone is produced when the calcium salt is distilled, and no anhydride is obtained by the distillation of the acid. It is slightly soluble in water at the ordinary temperature, and has a great tendency to form supersaturated solutions (Dieterle and Hell, Ber. 17, 2221); readily soluble in hot alcohol and ether. It forms salts with most metals which are generally soluble in water and crystallisable. There are eight isomerides of adipic acid, all of which have been prepared.

ADIPOCERE (from *adeps*, fat; and *cera*, wax). A peculiar waxy-looking substance, first observed by Fourcroy in 1786, when the *Cimetière des Innocents* at Paris was cleaned out. A large number of coffins had been piled together and had remained for many years; the corpses in many of these were converted into a saponaceous white substance. Fourcroy placed this substance, together with cholesterol and spermaceti, in a separate class termed by him 'Adipocere.' Gregory (Annalen, 1847, 61, 362), observed a similar substance in the case of a hog which had died of an illness, and had been buried on the slope of a mountain-side. The substance was completely soluble in alcohol, contained no glycerides, and consisted, according to Gregory, of about 25 p.c. of stearic acid, and about 75 p.c. of palmitic and oleic acids (these three acids form the chief constituents of lard). The absence of lime was explained by Gregory as due to the solvent action of water saturated with carbonic acid, which continually ran over the carcase. Gregory fully recognised that the fatty acids had been formed by the hydrolysis of the fat, water having washed away all the glycerol simultaneously produced, and he clearly stated his view that from corpses of animals all nitrogenous and earthy constituents could be washed away, fatty acids only remaining behind. Ebert (Ber. 8, 775) in the main confirmed these results in the examination of a specimen of adipocere. On saponifying with potash, about 1 p.c. ammonia escaped and an insoluble residue (about 6 p.c.), consisting of lime, &c., from tissues, remained. A mixture of potassium salts was obtained, which by fractional precipitation with magnesium acetate yielded mainly palmitic acid. The last fraction, not precipitable by magnesium acetate, but by lead acetate, yielded a hydroxylated acid, the formula of which is given as $C_{17}H_{34}O_3$. This acid, termed by Ebert hydroxymargaric acid, melts at 80°, and is most likely 1:10 hydroxystearic acid of the melting-point 81°. The occurrence of this acid in the adipocere examined by Ebert is very likely, as he could not detect any oleic acid; it would thus appear that in the course of time the oleic acid had been oxidised to 1:10 hydroxystearic acid. More recently Schmelck (Chem. Zeit. 1902, 11) found in the examination of three specimens of adipocere the following results:—

Melting-point . . .	62·5°C.
Insoluble fatty acids .	83–84 p.c.
Ash	1·7 p.c. (containing 83·5 p.c. CaO)
Unsaponifiable matter	16·7 p.c.
Acid value	197
Neutralisation value of the fatty acids . .	203
Iodine value . . .	14

Tarugi (Gazz. chim. ital. 34, ii. 469) also states that adipocere consists chiefly of palmitic acid.

The formation of adipocere from animal matter had been studied in glass vessels filled with water by Kratter. Kratter's opinion that adipocere originates from the albuminoids must, however, be rejected as erroneous, for there can be no doubt that the free fatty acids are formed by the hydrolysis of the body fat. All the decomposition products of the albuminoids and the glycerol would be washed away, and the fatty acids would naturally form with the lime of the bones, lime soap, which may or may not be further hydrolysed by water, to free acid and lime, according to the conditions obtaining in the decomposition of the body. There can be little doubt that the hydrolysing action of the water is greatly assisted by the presence of enzymes which act as accelerators in the hydrolytic action of the water on the body fat.

J. L.

ADONIN *v.* GLUCOSIDES.

ADONITOL *v.* CARBOHYDRATES.

ADRENALINE. *Epinephrine, Suprarenine* $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NH \cdot CH_3$. It may be obtained by extracting finely divided suprarenal glands with trichloracetic acid, concentrating the extract under reduced pressure and precipitating the adrenaline by the addition of ammonia (Abel, Ber. 1903, 1839; 1904, 368). Takamine (Chem. Soc. Abstr. 1903, i. 376, D. R. P. 131496) obtains a concentrated aqueous solution of the glands, renders it alkaline and precipitates the adrenaline by the addition of an ammonium salt or by passing carbon dioxide through the solution. The crude product is recrystallised from hot water. The constitution of adrenaline has been investigated by Jowett (Chem. Soc. Trans. 1904, 192), Bertrand (Compt. rend. 1904, 139, 502), Abderhalden and Bergell (Ber. 1904, 2022), and Böttcher (Ber. 1909, 253). Adrenaline has been synthesised from catechol. Catechol is treated with chloracetylchloride, and the resulting chloracetylcatechol condensed with methylamine, whereby monomethylaminoacetyl catechol is produced. Reduction of this with aluminium in the presence of mercuric sulphate yields adrenaline (Stolz, Ber. 1904, 37, 4149; Farb. Meister, Lucius and Brüning, D. R. PP. 152814, 155632, 157300; Chem. Zentr. 1904, ii. 270, 1487; 1905, i. 315. Other syntheses, *v.* Barger and Jowett, Chem. Soc. Trans. 1905, 967; Farb. Meister, Lucius and Brüning, D. R. P. 212206, Chem. Zentr. 1909, ii. 486; Böttcher. Ber. 1909, 42, 253; *cf.* Paulz, Ber. 1909, 42, 484). An aqueous solution rapidly oxidizes, becoming pink and finally brown (Takamine, Amer. J. Pharm. 1901, 73, 523). Fusion with potash converts adrenaline into catechol; potassium permanganate oxidises it to formic acid, oxalic acid, and methylamine (Jowett, *l.c.*).

Adrenaline is a very strong hæmostatic agent and an intravenous injection produces an enormous rise in blood pressure. The following reactions serve for its detection: (i.) a few drops of 1 : 1000 solution added to a solution containing copper sulphate and potassium cyanide give a characteristic red colour (Knill, Pharm. Zeit. 1907, 25, 115); (ii.) a characteristic odour resembling phosphoretted hydrogen is obtained by adding a few drops of adrenaline solution to a little sodium hydroxide (Gunn and Harrison, Pharm. J. 1907, 78, 718); (iii.) a fine red colour is obtained by boiling a solution containing a little potassium iodate and a few drops of phosphoric acid with a few c.c. of the adrenaline solution. Adrenaline may be estimated colorimetrically by means of iodine and sodium thiosulphate (Abelous, Soulié, and Toujan, Bull. Soc. chim. 1905, 23, 624).

ADSORPTION *v.* COLLOIDS.

ADUROL. Trade name for a haloid substitution product of hydroquinone, used as a photographic developer.

AËRATED OR MINERAL WATERS.

Originally the term 'mineral water' was used to describe natural spring waters containing small quantities of various salts in solution, and frequently saturated with carbon dioxide, hydrogen sulphide, or other gases. When these waters were first imitated by the artificial introduction of carbon dioxide into dilute saline liquids, they were known as 'aërated waters,' to distinguish them from the natural products. At the present time the two terms are employed indiscriminately, and as a rule the whole of the products of the manufacturer of aërated waters are popularly known as 'mineral waters.'

Natural Mineral Waters. In every quarter of the globe natural spring waters containing salts with medicinal properties are common, though fashion has made some more celebrated than others. Some of these waters (*e.g.* Hunyadi Janos) contain magnesium and sodium sulphate, and have an aperient action, whilst others containing iron (*e.g.* Tunbridge Wells water) are valued as tonics. Others, again, like the waters of Harrogate, contain sodium sulphide (0·02 p.c.), and are used as remedies in various complaints.

The most widely consumed natural mineral waters are those which contain only a small proportion of salts and a large amount of carbon dioxide. Typical examples of these are Apollinaris water, Selters water, and St. Gaulmier (French).

The table of analyses (p. 50) show the chief constituents of typical natural mineral waters.

Small quantities of many other compounds are also present in all these waters, but the figures given above represent their main constituents. The composition of all natural mineral waters varies from time to time, but they preserve their general characteristics.

Artificial Mineral Waters. Special mixtures of salts approximately corresponding in composition to those in many of the well-known medicinal waters are now sold, with directions for preparing solutions, which, when aërated, shall produce passable imitations of the natural products.

Among the purely artificial mineral waters mention must be made of *seltzer water*, which is prepared somewhat upon the lines of the natural Selters water, and contains sodium carbonate, chloride, and sulphate, and sometimes calcium and magnesium chlorides, the proportion of these ingredients being varied to suit the popular taste of the district. It is bottled at a pressure of about 120 lbs., corresponding to about 45–55 lbs. in the bottle.

Other medicinal artificial mineral waters include soda-water, potash-water, lithia-water,

PRINCIPAL SALINE CONSTITUENTS OF MINERAL WATERS—PARTS PER 10,000.

Source	Sodium carbonate	Sodium chloride	Sodium sulphate	Potassium carbonate	Potassium chloride	Potassium sulphate	Magnesium carbonate	Magnesium sulphate	Calcium carbonate	Iron oxide and alumina	Carbon dioxide per litre	Authority
											c.c.	
Apollinaris .	12·57	4·66	3·00	trace	—	—	4·42	—	0·59	0·20	—	Bischoff and Mohr
Hunyadi Janos	7·96	13·05	159·15	—	—	0·85	—	160·16	9·33	0·04	—	Knapp
Kissingen .	0·04	74·21	2·28	—	0·32	—	2·10	—	7·74	0·24	1026 at 11°C.	Kastner, Bauer, and Struve
Selters . .	8·01	22·51	—	—	0·47	0·51	2·60	—	2·43	—	1087 at 15°C.	Struve
Vichy . .	48·83	5·34	2·91	3·52	—	—	3·30	—	4·34	trace	508	Bouquet
Wiesbaden .	—	68·35	—	—	1·46	—	—	—	4·18	—	200	Fresenius

and magnesia-water. Soda-water was an official drug in the London Pharmacopœia of 1836, but was not introduced into the British Pharmacopœia until 1867. In the present Pharmacopœia (1898) it is omitted, together with the other alkaline waters. There is thus now no standard for soda-water, and since the old standard of 30 grains of sodium bicarbonate to the pint is sometimes found too alkaline to be palatable, a large proportion of the soda water upon the market contains much less than the old specified proportion of alkali.

Methods of Aërating.—The process of impregnating water with carbon dioxide under pressure dates back to the middle of the 18th century, one of the earliest inventors of apparatus for the purpose being the Duke de Challons in France. In this country the artificial 'aëration' of water was suggested by Bewley in 1767, and in 1772 Priestley constructed an apparatus somewhat on the principle of the modern Kipps' gas generator. A similar apparatus was devised about the same time by Bergman, and was extensively used throughout Sweden.

The earliest processes of bottling aërated waters made use of what is known as the 'Geneva' or *semi-continuous* process, in which the carbon dioxide, after being generated from chalk and acid, was forced under pressure with water into a cylinder, whence it could be drawn off into the bottles. This process, which is still employed in modified forms, is useful when a relatively small amount of liquid is to be impregnated, but has the drawbacks of requiring the work to be interrupted to recharge the cylinder, and of bottling the liquid at lower pressures than are often required. Hence in most mineral-water factories the *continuous process* is employed. Although numerous patents in connection with aërating machinery have been taken out, the type of machine which originated with Bramah is still the one in general use.

In Bramah's continuous process the gas is generated in a leaden or lead-lined generator from sulphuric acid and a carbonate, and passes into a gasometer consisting of an inverted copper bell in a tank of water. Thence, after expanding, it is pumped, simultaneously with water, into a condenser or globe, where the water is finely divided and saturated with the gas under a pressure indicated upon a gauge. From this it passes into the bottling part of the machine, where each bottle, placed by hand in position, receives a measured quantity of concentrated sodium carbonate solution or of sweetened syrup and is filled up with the water charged with the gas.

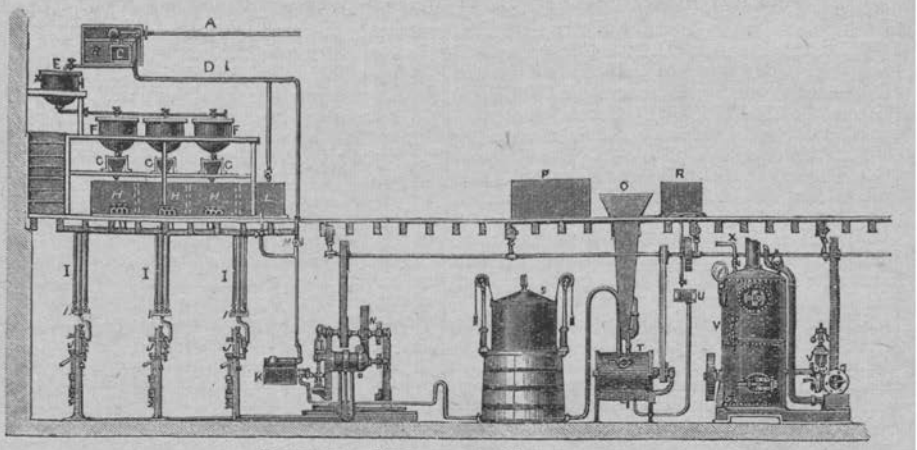
A 'blow-off' valve is provided so that the air may be completely expelled from the bottle, and in some types of machines there are means for returning the excess of gas to the gasometer, though this is not altogether advantageous.

Arrangement of Apparatus.—The general mode of arranging the aërating apparatus in the factory is shown in the accompanying figure (p. 51). The generator, T, is now frequently replaced by cylinders of liquefied carbon dioxide, which are connected with the gasometer. The soda-water machine, properly so called, has one or two pumps for forcing the gas and the water into the condenser, O, the latter being made of gun-metal with a lining of pure tin, and capable of withstanding a pressure three or four times in excess of any normally employed. In small installations a gas-engine usually takes the place of a steam-engine.

Carbon Dioxide Supply.—The general use of liquefied carbon dioxide instead of that generated from acid and calcium carbonate is the chief improvement on the original method of bottling. The new method is less expensive, more convenient, and obviates the difficulty attending the older process of disposing of the residue of calcium sulphate from the generator.

Liquefied carbon dioxide collected from the fermenting tuns in breweries is sometimes employed, but in the writer's experience gas from this source not infrequently contains traces of volatile impurities, which impart an unpleasant flavour to soda-water.

Pressures for Aërating.—Soda-water and similar unsweetened mineral waters are usually bottled at a pressure of 100–120 lbs. to the square inch in bottles, and of 150 lbs. in siphons, whilst for lemonade and the like a pressure of 60–80 lbs. is employed. In the case of goods intended for export a much lower pressure (usually 40–50 lbs.) is generally considered sufficient. The figures here given are those indicated upon the pressure gauge of the machine, the



PLAN OF A SODA-WATER MANUFACTORY.

A. Main water supply from well or waterworks.
B. Water reserve.
C. Filter.
D. Pipe and branches supplying filtered water to syrup boiler, solution tank, and soda-water machine.
E. Steam-cased pan for boiling syrups.
FFF. Mixing and cooling pans for syrups.
GGG. Felt filtering bags, through which syrup is passed.
HHH. Tank in compartments for storing filtered syrups.
III. Syrup junctions and pipes supplying syrup pumps at bottling machines.
JJJ. Bottling machines
K. Solution pan feeding soda-water machine with either plain water from filter C, or soda or other solution from tank L.
L. Soda-water solution tank for mixing mineral waters which require no syrup. When using this tank the tap M is closed.
M. Tap to shut off plain filtered water when bottling non-saccharine beverages.
N. Soda-water machine.
O. Condenser containing aërated water, to which pipes leading to bottling machines are attached.
P. Whiting bin.
Q. Whiting shoot to generator.
R. Vitriol cistern.
S. Gasometer.
T. Generator.
U. Blow-back prevention acid box.
V. Steam engine.
X. Steam pipe to syrup boiler and bottle-washing apparatus.

actual pressure in the closed bottle being very much less. Thus experiments made by the writer have shown that the pressure within bottles of soda water bottled at a machine pressure of 100–120 lbs. does not exceed 45–55 lbs. An excess of pressure above a certain limit does not result in the liquid containing more gas.

An essential of good bottling is that all air should be expelled from the bottle, since otherwise, air being only slightly soluble as compared with carbon dioxide, the liquid will rush with almost explosive violence from the bottle, when opened, but will become flat almost immediately. On the other hand, a liquid properly saturated with carbon dioxide and free from air will continue to emit minute bubbles of gas for at least five minutes after it leaves the bottle.

Pressure Gauges.—The mode of measuring the pressure of the gas varies in different countries. Thus in England and the United States the zero mark on the dial of the pressure gauge indicates atmospheric pressure, and the succeeding figures represent the number of lbs. in *excess* of that pressure. In Germany the dial is graduated in atmospheric pressures in excess of the normal pressure, which is represented by zero; whereas in France, which adopts the same mode of expression, the figure 1 represents the normal pressure, and the figure 2 corresponds to 1 on the German scale and to 15 lbs. on the British and American scales, and so on.

Sweetened Aërated Drinks.—Lemonade, ginger ale, and similar sweetened 'mineral waters' are prepared in the same way as soda water. A thick syrup is made from sugar and saccharin and water, and this is acidified with citric or tartaric acid and flavoured with an essential oil, which is conveniently added in the form of an alcoholic solution termed a 'soluble essence.'

The syrups are filtered through the filter bags shown at C, C, C, in the diagram, into their respective tanks, H, H, H, whence they are drawn off into the bottling machine. The use of saccharin to replace part of the sugar in the syrups is almost universal in this country. It has the advantages of reducing the cost and of acting as a preservative, whilst its disadvantages are its cloying taste, which prevents its being used in more than a certain proportion, and the want of fulness on the palate of syrups containing it. The latter drawback is sometimes remedied by the addition of glucose syrup.

Methods of detecting and identifying saccharin are described by Boucher and Boungne, Bull. Soc. Chim. Belg. 1903, 17, 126; Analyst, 1903, 28, 241; von Maler, Farmaz. J. 1904, 1089; Analyst, 1904, 29, 374; Villiers, Ann. Chim. Anal. 1904, 9, 418; Analyst, 1905, 30, 21; Chace, J. Amer. Chem. Soc. 1904, 26, 1627; Jorgensen, Analyst, 1909, 34, 156.

Addition of Saponin.—The popular demand for a liquid which shall retain a frothy head for some time after it has left the bottle has led to the manufacturers frequently adding an extract of quillaia bark or other preparation of saponin, sold under the name of 'foam heading,' &c. Such an addition is more necessary in liquids containing saccharin than in all-sugar beverages, which froth more with the carbon

dioxide. According to the results of experiments made by Lohmann (Z. öffentl. Chem. 1903, 9, 320; Analyst, 1903, 28, 361), saponin has no injurious physiological effects. On the other hand, according to Bourcet and Chevalier (Pharm. J. 1905, 75, 691) commercial saponin contains neutral saponins of a toxic nature.

For the detection of saponin, see Brunner (Zeit. Untersuch. Nahr. Genussm. 1902, 5, 1197) and Rühle, *ibid.* 1908, 16, 165 (J. Chem. Soc. Ind. 1908, 27, 954).

Fermented Beverages.—The products of the mineral water factory include one or two beverages in which the aëration is the result of a limited fermentation.

Ginger beer, which is the type of this class, is prepared by adding sugar and citric acid to a dilute infusion of ginger root, infecting the liquid with a small quantity of a suitable yeast, bottling it, and allowing the bottles to stand at a proper temperature until sufficient fermentation has taken place.

As a rule the fermented liquid contains less than 1 p.c. of absolute alcohol, but occasionally in very hot weather the fermentation may proceed much further, and the ginger beer may then contain as much as 5 or 6 p.c. of alcohol. The pressure in the bottle of ginger beer when ready for consumption averages about 15 lbs. to the square inch, but in cases of abnormal fermentation it may reach 100 lbs. or more, and burst the bottle.

Occasionally objectionable flavours are produced by infection of the liquid with wild yeasts or bacteria, just as in the case of ordinary beer.

Other drinks of this description are horehound beer and other herb beers. Certain non-alcoholic ales on the market are prepared by partial fermentation of an infusion of malt and hops, which is then used as a syrup, and bottled with aërated water as in the case of lemonade.

Stoppers of Bottles.—The screw stopper of vulcanite or stoneware with a rubber ring to effect a tight joint is now universally employed; for the glass ball-stopper (which had much to recommend it) has fallen into popular disfavour, and is now rarely met with, except in out-of-the-way districts.

The chief objection to the rubber-clad stopper is that impurities of various kinds may lodge beneath the rubber, and unless strict cleanliness is observed, may contaminate the contents of the next bottle into which it is introduced.

Bacteriological Conditions.—Until about two or three years ago it was commonly believed that sterilisation was effected by aërating a liquid with carbon dioxide under a high pressure. In 1908, however, bacterioscopic examinations were made, at the instigation of the medical officer for the City of London, of a large number of bottles of soda-water, and it was found that about 25 p.c. could be regarded as pure, and over 33 p.c. as impure, the remainder being 'fairly pure' or 'not pure.' In some of the worst samples the numbers of micro-organisms per 1 c.c. at 20° were uncountable, and some yielded sediment from 50 c.c., which when cultivated at 37°, gave innumerable colonies.

As the result of this investigation a meeting of representative mineral water manufacturers was held, and it was decided to adopt stringent measures to guard against bacterial contamination.

In addition to the obvious precautions of having a pure water supply and observing cleanliness in every stage of the manufacture, it was agreed to discard all wooden tanks and vessels (except for preliminary soaking to remove labels from old bottles), to rinse the bottles with water of assured purity immediately before filling, and to use for this purpose a metal jet of sufficient force. Wherever practicable, rubber rings were to be removed from the stoppers, or, failing that, were to be immersed in a solution of calcium bisulphite, and afterwards rinsed with pure water. The plant was also to be inspected by a competent authority.

There is no doubt that the adoption of such precautions has had the result of raising the standard of purity of soda-water throughout the country.

In considering the bacteriological aspect of the question, several points suggest themselves. Thus an unfavourable bacterioscopic examination of one or two samples taken casually does not necessarily imply faulty manufacture, for it may be the result of accidental contamination of the stopper by the hands of the worker—against which there is no complete safeguard.

Absolute sterility of the contents of the bottle should not be demanded, and it is unreasonable to require a greater degree of purity than that of the average water supply of London. Given a sufficient degree of purity of the original water, which is essential, efficient inspection of the factory at irregular intervals is a better protection than an occasional bacterioscopic examination. When such examinations are made periodically, they should be made under comparable conditions, *i.e.* at the same intervals after bottling; otherwise the product of the cleaner process may show the worse results.

Standards are notoriously difficult to fix, but making allowance for the various chances of contamination, an average sample of soda water, examined one day after bottling, should not yield more than 100 organisms per 1 c.c. at 20°, or contain sufficient *B. coli* to be discoverable in 10 c.c.

Preservatives in Mineral Waters.—The preservatives most likely to be met with in unsweetened mineral waters are sulphites and bisulphites, solutions of which are frequently used, as in breweries, for cleansing the plant.

A small proportion of salicylic acid is often employed to prevent fermentation in the so-called 'fruit syrups' and other sweetened articles, which might otherwise ferment and be the subject of an excise prosecution for containing alcohol.

Fermentations occurring in Mineral Waters.—Excessive fermentation of ginger beer is not uncommon in very hot weather, and the writer has met with samples containing as much as 6 p.c. of absolute alcohol.

Occasionally acetic or lactic fermentation may take place, and spoil a batch of goods, but this seldom happens when thorough cleanliness is observed.

A troublesome form of fermentation, commonly termed the 'mucoid fermentation,' results in the conversion of the contents of the bottle into

a thick ropy gelatinous mass. This may be caused by several micro-organisms, such as *B. gelatinosum betæ* or *B. viscosus sacchari*, and is more liable to occur when beet sugar is used for the syrup than when cane sugar is used. When it occurs in an isolated bottle, insufficient cleansing is a chief factor in its production.

Metallic Impurities.—Mineral waters not infrequently contain traces of metallic impurities, especially iron, tin, and lead, derived from the materials used or from some part of the plant.

Iron in soda-water is objectionable from the fact that, when the beverage is added to a light-coloured liquid, such as whiskey, containing a trace of tannin, an unpleasant dark colouration is produced.

Traces of tin find their way into mineral waters through the action of acid syrups upon the tin piping leading to the bottling machines, whilst lead may be derived from solder on the pipes. No such soldering should be permitted, and thorough flushing of tin piping with water night and morning effectually prevents contamination with tin. A still better safeguard, which has been adopted by some factories, is to replace the tin pipe by glass tubes with rubber connections.

A still more common source of lead is the citric or tartaric acid, in which it is frequently present as a manufacturing impurity.

Copper is not a common impurity, and, when present, is usually due to accidental contact of the acid syrup with the metal.

Arsenic may be derived from glucose used in the preparation of the syrups, or from the use of preparations of phosphoric acid instead of citric or tartaric acid for acidifying the syrups.

It has been asserted that mineral waters take up traces of antimony from the rubber rings of the stopper (which contain a large proportion of antimony sulphide). Experiments made by the writer, however, have shown that even a boiling 5 p.c. solution of hydrochloric acid does not dissolve any antimony from red rubber, and that there is thus no risk of mineral waters being contaminated in this way.

(For the detection of traces of metallic impurities in mineral waters, *see* Budden and Hardy (Detection of Lead, Tin, Copper, and Iron), Analyst, 1894, 19, 169; Tatlock and Thomson (Lead in Citric and Tartaric Acid), Analyst, 1908, 33, 173; Lander and Winter (Poisonous Metals), Analyst, 1908, 33, 450; Report of Conjoint Committee on Arsenic Determination, Analyst, 1902, 27, 48; Report of Royal Commission (Arsenic), Analyst, 1904, 29, 60; Thorpe (Electrolytic Determination of Arsenic), Analyst, 1903, 28, 349). C. A. M.

ÆRUGO. (Verdigris (?) or basic carbonate of copper.) The name given by the Romans to the green rust produced on copper and bronze by the united action of the oxygen and carbon dioxide of the air. It was considered by them to enhance the beauty of their bronze statues. The same rust forms on brass, which was, however, not used by the Romans.

ÆSCULIN *v.* GLUCOSIDES.

AETHUSA CYNAPIUM (Linn.). 'Fool's parsley' or the 'lesser hemlock,' a poisonous umbelliferous herb. When dried and extracted with alcohol, yields on distillation a small quantity of an essential oil, and the residue contains a resin, a crystalline hydrocarbon *pentatriacontane* $C_{35}H_{72}$ (m.p. 74°) and a crystalline alcohol (m.p. 140°–141° : $[\alpha]_D = -35{\cdot}7°$) either isomeric with phytosterol $C_{26}H_{44}O$, or a lower homologue; *d-mannitol*, together with a small quantity of a *volatile alkaloid* resembling conine, to which the alleged poisonous character of the herb may be due (Power and Tutin, J. Soc. Chem. Ind. 1905, 938).

AFFINITY, CHEMICAL *v.* CHEMICAL AFFINITY.

AFRICAN ELEMI *v.* OLEO-RESINS.

AFRICAN GREEN or **EMERALD GREEN** *v.* PIGMENTS.

AFRICAN INCENSE *v.* OLEO-RESINS.

AGALITE. A name used in the paper-making trade for a fibrous variety of the mineral talc, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$. It is white with a tinge of green, and is readily reduced to short, fine fibres. It is obtained almost exclusively from the district near Gouverneur, in St. Lawrence Co., New York, about 70,000 tons, valued at $10 per ton, being produced annually. With the exception of a small quantity exported to Germany, it is all used in the American paper trade. It gives weight and body, and produces a fine gloss on the surface of the paper. L. J. S.

AGALMATOLITE, or Pagodite. A soft stone much used in the East, especially in China, for carving small statues and figures, as signified by these names. At least three mineral species appear to be included under these terms, viz. pyrophyllite, steatite, and pinite; but it is to the compact forms of the first of these that they are perhaps more generally applied. In addition to their compact nature and low degree of hardness, they have in common a greasy or soapy feel: in colour they are white, greyish, greenish, yellowish, &c., often with mottling. Pyrophyllite is a hydrated aluminium silicate, $H_2Al_2Si_4O_{12}$; steatite, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$; and pinite is an alteration-product consisting largely of a finely scaly muscovite-mica, a hydrated potassium aluminium silicate, $H_2KAl_3Si_3O_{12}$. Besides being employed as material for carving, these minerals are used for slate-pencils ('pencil-stone') and for tailor's chalk ('French chalk').

Extensive beds of compact pyrophyllite are quarried in the Deep River region in North Carolina, the material being mainly used for making slate-pencils. At Fukuye, in Goto Island, in the south of Japan, a compact mineral allied to pyrophyllite is mined under the name of 'rōseki' (meaning 'greasy stone' in Japanese); it is crushed, washed, and prepared very much like china-clay, and the product used for making fire-bricks, and to a smaller extent in the manufacture of porcelain and paper. This material contains SiO_2 53–58, Al_2O_3 32–36, H_2O 7–9 p.c. L. J. S.

AGAR-AGAR. Bengal Isinglass. Dried seaweed obtained from Singapore. It is obtained from various red algæ, including *Gelidium corneum*, *G. cartilagineum*, *Eucheuma spinosum*, and *Gracilaria lichenoides*, which grow along the coasts of Eastern Asia and Malaya. The cell-walls of these seaweeds, when placed in boiling water, change into jelly.

It occurs in small transparent strips or as

a powder, and dissolves almost entirely in water to a gelatinous, tasteless, and inodorous jelly. It is widely used as a nutritive medium for the cultivation of bacteria and fungi (*v.* ALGÆ).

AGAROBILLA. The seed-pods of *Cæsalpina brevifolia* (Baill.), used in dyeing and tanning.

AGATE. (*Achat*, Ger.) A natural aggregate of various forms of crystalline, crypto-crystalline, and colloidal silica. In most agates these siliceous minerals are arranged in alternating layers, which present on section a banded appearance, whence the agate is valued, when cut and polished, as an ornamental stone. This zoned structure is usually the result of the deposition of silica in successive layers within the cavities of a vesicular rock. In some cases, however, the deposition has been effected in fissures, thus forming siliceous veins, as in the brecciated agates of Saxony and Bohemia. In other cases the agates may occur in the cavities of stratified rocks, or occupy the spaces between the pebbles of a conglomerate: such are the agates of the dolomitic conglomerate and the 'potato stones' of the Triassic marls of Somersetshire.

The artificial deposition of silica, in forms closely resembling those of certain agates, has been effected by I'Anson and Pankhurst (Min. Mag. v. 1882, p. 34). A strong acid is introduced by means of a pipette into a solution of an alkaline silicate, containing a certain proportion of alkaline carbonate; the bubbles of carbon dioxide set free become coated as they ascend with gelatinous silica, which forms a tube; and by continued deposition a stalactiform agate is produced. If a cavity in a rock were filled with a solution of an alkaline silicate, and the rock permeated by an acid, a layer of amorphous hydrated silica would be deposited upon the walls of the cavity, and through this gelatinous layer further deposition might gradually proceed.

The rocks in which agates typically occur are the basic igneous rocks known as basalt, dolerite, diabase, and melaphyre. These 'traps' are essentially plagioclase-augite rocks. In many cases they present a vesicular texture, and the vesicles may enclose various secondary minerals resulting from the decomposition of the constituents of the rock. Among the commonest of these alteration-products is the green earthy mineral known as *delessite*, a hydrated silicate of aluminium, iron, and magnesium, probably a product of the decomposition of the augite. Many vesicles are simply lined with this green substance, but in other cases the delessite becomes covered by subsequent mineral deposits until the cavities are more or less completely filled. The rock thus becomes 'amygdaloidal,' a term suggested by the fact that the kernels of mineral are usually of almond-like shape. This shape is due to the cavities, which were originally gas- or steam-bubbles, having been elongated by the flow of the lava-like rock when viscous. In many cases the 'amygdules,' or contents of the cavities, are kernels of calcite, but in other cases they are siliceous. If hollow they form *geodes;* and when nearly filled with alternate layers of chalcedony, jasper, quartz, and other forms of silica, they constitute true agates.

The embedded agates are easily detached from the enclosing rock, and when removed usually present a pitted surface. On the exterior is a green coating or 'skin' of delessite, or of the similar mineral *chlorophæite:* many of the larger agates, however, present a rusty coating of ferric hydrate. The earliest-formed siliceous deposits are usually chalcedonic, and the latest are often crystalline: thus in a hollow agate the interior is generally lined with a crop of quartz crystals, not unfrequently amethystine, the apices of the pyramidal crystals being directed towards the central cavity. This structure shows that the agate has been formed by successive deposition from without inwards: in other words, the growth has been 'endogenous.' It is notable that in certain agates the first-formed layers have been concentric with the walls of the original cavity, and the subsequent strata horizontal.

Tubular orifices, lined with siliceous deposits, may be detected in many agates, and these have been commonly regarded as inlets of infiltration, or channels through which the siliceous solution gained access to the interior. It has, however, been held by many observers that the solution, so far from having been introduced through a definite aperture, gradually filtered in at all points; and the internal walls thus became uniformly coated with a gelatinous layer, which allowed the further introduction of silica by osmotic action. Heddle pointed out that if, by a difference in the density of the siliceous solutions within and without the cavity, pressure were exerted outwards against the gelatinous medium, this deposit might give way, and the so-called inlet would thus be really a point of egress (Nature, 1884, p. 419). E. Reusch has suggested that the agate-bearing cavities were filled periodically with hot siliceous solutions by the action of intermittent thermal springs (Pogg. Ann. 1864, p. 94). G. Lange, extending this view, supposes that the steam from the solution confined in the cavity might exert sufficient pressure outwards to pierce the gelatinous deposit, and thus an outlet of escape might be mistaken for an inlet of infiltration.

Agates, when released from their matrix by its natural disintegration, occur as loose nodules, either in the beds of rivers or scattered over the country in pebble-drifts. The 'Scotch pebbles' are found chiefly near Montrose in Forfarshire, and at the Hill of Kinnoul in Perthshire. The agates of the Cheviots are found in the Coquet and other Northumbrian rivers. In India agates have for ages been worked by the lapidaries of Cambay, Broach, and Ratanpur, who obtain their supply from the traps of the Deccan and of the Rájmahál Hills, or from the agate-bearing gravels of Rajpipla, which are systematically mined (Man. Geol. India, pt. III. [V. Ball], 1881, p. 503; pt. IV. [F. R. Mallet], 1887, p. 70).

The largest and finest agates are the so-called Brazilian stones, which come chiefly from the State of Rio Grande do Sul in Brazil, and from the neighbouring country of Uruguay. Here they are mostly found as pebbles in the beds of rivers, especially the R. Taquarie, having been derived from amygdaloidal trap rocks. Some interesting agates have been obtained from Uruguay, consisting of a rind of chalcedony, lined with quartz crystals, and containing liquid, movable within. These have been called *water-stones, hydrolites,* or

enhydros. According to C. W. Gümbel, the liquid is water with a small quantity of NaCl, $CaCl_2$,$CaSO_4$,SiO_2,CO_2, &c. (Sitz. B. z. München, 1880, II. p. 241; 1881, III. p. 321). Chalcedonic waterstones, of polyhedral form, occur at Beechworth, Victoria.

Moss-agate consists of chalcedony enclosing twisted filaments, usually green but sometimes red or brown, resembling vegetable structures. *Mocha-stones* are simply white or brown chalcedony, generally from India, with dendritic or arborescent markings due to oxides of iron and manganese. *Fortification-agate* is a term applied to those stones in which strata of jasper and chalcedony have been deposited upon quartz crystals, and hence they present on section curious zigzag patterns, suggestive of the plan of a fortress. The trivial terms *eye-agate*, *riband-agate*, &c., need no explanation.

Agate is employed for the knife-edges of balances, for small mortars and pestles, for burnishers and writing styles, for trinket-boxes, umbrella-handles, seals, brooches, beads, and an endless variety of trivial ornaments. Nearly all the agate used in the arts is worked in Germany.

The industry of cutting and polishing agates is centred in the neighbourhood of Oberstein on the river Nahe, a tributary to the Rhine at Bingen. Most of the agate-mills are situated near Idar, about two miles north of Oberstein. Here the Idar Bach, which flows into the Nahe, furnishes abundant water-power, which for four centuries has been utilised in the local mills. The original location of the trade in this district was due to the occurrence of agates in the amygdaloidal melaphyre of the Galgenberg, near Idar, where agates were formerly obtained by systematic mining operations. For many years, however, these workings have been abandoned, and the mills have been supplied with South American agates, the importation of which was begun about 1827.

Large consignments of South American agates are periodically sold by auction at Oberstein. The common stones are first roughly dressed with hammer and chisel, while the finer stones are carefully wrought into form by means of metal discs fed with emery or with diamond powder. The grinding is performed on wheels of red sandstone, about 5 feet in diameter, set vertically, and rotating at the rate of about three revolutions per second. Each stone is about 1 foot in width, and its surface presents channels corresponding with the form of the objects to be ground. The stones are usually moved by large undershot water-wheels, but the inconvenience of their stoppage during the drought of summer or the frost of winter has led to the partial introduction of steam-power. When working, the grinder lies almost horizontally upon a wooden stool, hollowed to the shape of his body, and having his arms free. The agate is pressed forcibly against the grindstone, fed with water from above, while the workman obtains purchase by pressing his feet against a block fastened to the floor. The polishing is afterwards effected with rouge and water on soft metal plates or with tripoli on wooden cylinders.

Not only agates, but rock-crystal, amethyst, false crocidolite, and other hard stones are now extensively cut and polished by the Idar lapidaries. These stones are also cut, to a limited extent, at Waldkirch in the Black Forest.

For many years the German agate-workers, following the earlier practice of the Italian cameo-cutters, have modified the colour of most of the stones by staining them. The commonest practice is that of darkening certain layers in a banded agate, so as to produce an *onyx*. The onyx presents a succession of two or more strata, alternately light and dark brown, or even white and black. To produce this contrast of colour when not naturally present, the agate is first steeped in honey and water, and gently heated on a stove. In course of time, perhaps two or three weeks, certain layers of chalcedony, more porous than others, are found to have absorbed the saccharine matter. No perceptible change is observed when the agate is removed and washed; but on placing it for a short time in sulphuric acid the absorbed matter becomes carbonised, and it is then seen that certain layers of chalcedony, originally of a dull grey tint, have assumed a rich brown or even black colour. In place of the honey, olive oil is sometimes used. If accidentally coloured too strong, the excess may be removed, or the colour 'drawn,' by the use of nitric acid. The process of darkening agates is one of great antiquity, and is imperfectly described by Pliny (Hist. Nat. xxxvii. c. 75) as having been in his day practised in Arabia. On the history of colouring agates, *v.* Nöggerath, Die Kunst, Onyxe . . . zu färben, Karsten's Archiv. xxii. 1848, p. 262.

Carnelian is a red variety of chalcedony, and its characteristic tint may be easily developed artificially in the chalcedonic bands of certain agates which are, in their natural state, merely grey or yellowish. It has long been the practice in India to heighten the colour of pale brownish agates by prolonged exposure to solar heat, whereby any ferric hydrate in the stone loses more or less water. In Germany the agate is usually heated and then moistened with sulphuric acid, or is placed in a solution of ferric nitrate, prepared by throwing old nails into dilute aquafortis; in either case the stone is afterwards exposed to a red heat, whereby the absorbed salt is decomposed and ferric oxide formed. Alternating bands of red and white chalcedony constitute the variety of agate known as *sardonyx*, and it is to imitate this stone that the red tints are often developed. Prolonged digestion in warm hydrochloric acid imparts a yellow tint to the agate, but this colour is not popular. Green colours, resembling those of *chrysoprase*, which is simply a green chalcedony, are produced by means of salts of either nickel or chromium. Blue tints may be readily obtained by soaking the stone in a solution of ferrous sulphate and afterwards in either ferrocyanide or ferricyanide of potassium, when Prussian blue or Turnbull's blue is formed in the pores of the stone; or an ammoniacal solution of sulphate of copper may be used. Blue agates, artificially stained, are extensively sold as lapis-lazuli. More recently a dead-white effect has been produced in certain stones, which are thus rendered more valuable for cameo work. It is said that this effect is obtained by the use of caustic potash and subsequent exposure to a high temperature. On the agate industry, *v.* H. Lange, Die Halbedelsteine, Kreuznach, 1868;

Upmann, Beitr. z. Gesch. d. Graftsch. Oberstein, Mainz, 1872; M. Bauer, Edelsteinkunde, 2nd ed., Leipzig, 1909, and Engl. transl., Precious Stones, by L. J. Spencer, London, 1904.

F. W. R.

AGAVE. An amaryllidaceous genus including several species, the leaves of which provide useful fibres. 'Pite,' or 'pita hemp,' mainly produced in Mexico, is obtained from *A. americana* (Linn.) and *A. mexicana* (Lam.). It is also obtained from several other American species of *Agave*. 'Sisal hemp' is derived from *A. rigida* (Mill.), which grows in Mexico, Central America, and the West Indies.

AGAVOSE. An inactive sugar $C_{12}H_{22}O_{11}$, reducing alkaline copper tartrate, and yielding a lævogyrate sugar on inversion; found in *Agave americana* (Linn.), grown in Mexico. The young flower heads are used in the preparation of a fermented intoxicating drink termed 'pulque' (Michaud and Tristan, J. Amer. Chem. Soc. 14, 548). According to Stone and Lotz, J. Amer. Chem. Soc. 17, 368, this sugar is saccharose.

AGONIADA BARK. The bark of *Plumiera lancifolia* (Muell.), used in Brazil as a remedy for intermittent fever, contains a bitter crystalline glucoside, *agoniadin* (Peckolt, Arch. Pharm. [2] 142, 40, 1870), identical with the *plumieride* of Boorsma and Merck, obtained from *Plumiera acutifolia* (Poir.); it is probably the *methyl ester of plumieridic acid*, and has the composition $C_{21}H_{26}O_{12}$ (*cf.* Franchimont, Rec. trav. chim. 1898, 18, 334; Proc. K. Akad. Wetensch. Amsterdam, 1900, 3, 35).

AGROSTEMMA SAPOTOXIN *v.* GLUCOSIDES.

AICH METAL. An alloy patented by J. Aich in 1860 for use as sheathing for ships. Contains copper, 60 parts; zinc, 38·5 parts; iron, 1·5 parts.

AILANTHUS BARK. The inner bark of *A. excelsa* (Roxb.) and *A. glandulosa* (Desf.); it has the odour and taste of cinnamon; used as a tonic in dyspepsia (Dymock, Pharm. J. [3] 7, 309). An Indian name of the former is *Maharukh*.

AIROFORM. Identical with airol (*q.v.*).

AIROGEN. Identical with airol (*q.v.*).

AIROL. A basic bismuth-oxyiodide gallate, analogous to 'dermatol,' a basic bismuth-gallate. Is a greyish-green powder without smell or taste, soluble in caustic soda or dilute mineral acids. Becomes red on exposure to damp air. Has been used clinically as a substitute for iodoform (*v.* BISMUTH).

AKANDA *v.* AK MUDAR.

AK MUDAR, AKANDA, AKRA RUI, or ERUKKU ERUKKAM. The bark of *Calotropis gigantea* (Ait.) and *C. procera* (Ait.). An important Indian drug (Dymock, Pharm. J. [3] 10, 122).

AKOLA *v.* ANKOOL.

AKRA RUI *v.* AK MUDAR.

ALABANDITE. *Manganese sulphide* (MnS) (*v.* MANGANESE).

ALABASTER. (*Albâtre*, Fr.; *Alabaster*, Ger.) A massive, crystalline, and marble-like variety of the mineral gypsum ($CaSO_4,2H_2O$). It is found in Glamorganshire; at Syston in Leicestershire; at Tutbury, near Burton-on-Trent in Staffordshire, and other places in Britain. A snow-white alabaster much used for small ornamental objects, such as vases, lamps, stands of time-pieces, &c., is found at Volterra, in Tuscany. The harder varieties are worked with the same tools as marble, smoothed with pumice stone, polished with a mixture of chalk, soap, and milk, and finished by friction with a flannel.

The softer kinds may be turned or fashioned with rasping tools, fine chisels, or small files, smoothed with dried shave grass, then rubbed with a paste of putty powder or finely divided slaked lime, and polished by washing with soap, water, and lime, and finally with powdered elutriated French chalk or talc.

Alabaster may be stained by heating it to about 90° or 100°, and then dipping it into the colouring solution, which may be either metallic solutions, spirituous tinctures of natural dyes, or coloured oils (Habild, Wagner's Jahr. 28, 669).

A variety of alabaster known as onyx of Tecali, from Mexico, takes a fine polish; its colour varies from milk-white to pale-yellow and pale-green (J. 29, 1264).

ALACREATINE *v.* CREATINE.

ALAMOSITE. A lead silicate $PbSiO_3$, found near Alamos, Sonora, Mexico; analogous to wollastonite $CaSiO_3$ in form, habit, and composition. It occurs in radiated aggregates of minute colourless transparent fibres, which give a snow-white appearance to the mass (Palache and Merwin, Amer. J. Sci. 1909, 27, 399; J. Soc. Chem. Ind. 1909, 606).

ALANGIUM LAMARCKII *v.* ANKOOL.

ALANINE, *α*-**Alanine,** *α-aminopropionic acid* $NH_2{\cdot}CHMe{\cdot}CO_2H$, contains an asymmetric carbon atom, and the dextro-, lævo-, and racemic isomerides are known. *d*-Alanine is one of the decomposition products of a large number of proteids; together with a glucoproteid $C_7H_{14}O_4N_2$, it forms 51 p.c. of the product obtained by the hydrolysis of legumin of peas (Bleunard, Ann. Chim. Phys. [5] 26, 47), and is formed to the extent of 21 p.c. from silk fibroin (Weyl, Ber. 21, 1529; Fischer and Skita, Zeitsch. physiol. Chem. 33, 177). (For the methods of separating alanine from the other hydrolytic products of the proteid, *v.* art. PROTEINS.) *r*-Alanine is prepared synthetically by the action of hydrochloric acid on the aminonitrile $NH_2{\cdot}CHMe{\cdot}CN$, produced by the interaction of aldehyde ammonia on hydrogen cyanide (Strecker, Annalen, 75, 29); or, together with *α*-aminopropionitrile hydrochloride, when ammonium chloride, potassium cyanide, and acetaldehyde interact in equimolecular quantities in aqueous solution (Zelinsky and Stadnikoff, Ber. 41, 2061); or by reducing *α*-nitrosopropionic acid with tin and hydrochloric acid (Gutknecht, Ber. 13, 1116).

Alanine crystallises in needles or sharp rhombic prisms, dissolves in 4·6 parts of water at 17°, or in 500 parts of 80 p.c. cold alcohol; its heat of combustion is 389 Cal. and heat of formation 135·2 Cal. (Berthelot and André, Compt. rend. 110, 884). The resolution of racemic alanine has been effected through the benzoyl derivative, which is separated into *d-benzoylalanine* (m.p. 147°–148° $[\alpha]_D$ +37·13° in alkaline solution), and *l-benzoylalanine* (m.p. 150°–151° (corr.), $[\alpha]_D$ −37·3° in alkaline solution), by crystallisation of the brucine salt, and these yield on

hydrolysis the corresponding optically active alanines; *r-alanine* decomposes at 264°–268° (Zelinsky and Stadnikoff, *l.c.*), at 293° (Fischer, Ber. 32, 2451); *d-alanine* has $[\alpha]_D$ + 9·55° in hydrochloric acid solution; *l-alanine* decomposes at 297° and has $[\alpha]_D$ − 9·68° in hydrochloric acid solution. A cultivation of *Aspergillus niger* in an aqueous solution of *r*-alanine destroys about 10 p.c. of the dextrorotatory constituent, but *Penicillium glaucum* does not flourish in a 2 p.c. alanine solution.

In its physiological action, *d*-alanine causes a rapid rise in the urinary nitrogen, most of the extra nitrogen being excreted on the same day; *l*-alanine is not decomposed quite so rapidly, but none of it is excreted unchanged (Abderhalden and Schittenhelm, Zeitsch. physiol. Chem. 1907, 51, 323; compare, however, Sevene and Meyer (Amer. J. Physiol. 1909, 25, 214). After administering 20 grms. of *r*-alanine, 4·7 grms. of the β-naphthalenesulphonic derivative of *l*-alanine was recovered from the urine (Schittenhelm and Katzenstein, Chem. Zentr. 1906, i. 1279). When *d*-alanine is injected in the blood-stream it is rapidly absorbed, as very little can be detected in the blood or urine after a lapse of twenty minutes (Abderhalden and others, Zeitsch. physiol. Chem. 1907, 53, 113, 251, 326; 52, 507; 53, 148).

The importance of alanine as a final hydrolytic product of many proteid substances, has led to an extensive examination of its derivatives in order to facilitate its detection and estimation, and to determine the part it plays in the building up of the proteid molecule. A short account of the more important of these derivatives is appended.

The *copper salt* $(C_3H_6O_2N)_2Cu,H_2O$ forms bluish-violet crystals readily soluble in water. The *nickel salt* $(C_3H_6O_2N)_2Ni,4H_2O$ forms blue crystals, these become anhydrous at 108°–110° and dissolve in 132 parts of water (Orloff, Chem. Zentr. 1897, ii. 192; Bruni and Formara, Atti R. Accad. Lincei, 1904, [v] 13, ii. 26). The *ethyl ester* has b.p. 48°/11 mm. and sp.gr. 0·9846 at 12·5°; *r-alaninamide*, m.p. 62° (Franchimont and Friedman, Proc. R. Akad. Wetensch. Amsterdam, 1905, 8, 475); *d-alaninamide* has m.p. 72° (corr.) and $[\alpha]_D$ +6° in 5·2 p.c. aqueous solution; *r-alanylchloride hydrochloride* $NH_2Cl\cdot CHMe\cdot COCl$ melts and decomposes at 110°; *d-alanylchloride hydrochloride* has $[\alpha]_D^{20°}$ +7·32 (Fischer, Ber. 1905, 38, 605, 2914); *r-alanineanhydride* (*dimethyldiketopiperazine* $NH<\begin{matrix}CHMe\cdot CO\\CO\cdot CHMe\end{matrix}>NH$ has m.p. 282°, and *d-alanineanhydride* has m.p. 297° (corr.) and $[\alpha]_D^{20°}$ −28·8° (Fischer, Ber. 1905, 39, 453). *Acetylalanine* $NHAc\cdot CHMe\cdot CO_2H$ crystallises in rhombic plates $a:b:c=0{\cdot}7792:1:1{\cdot}0983$; m.p. 137° (de Jong, Rec. trav. chim. 19, 259; Fischer and Otto, Ber. 36, 2106); *chloracetylalanine ester* $CH_2Cl\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et$ has m.p. 48·5°–49·5° (corr.) (Fischer and Otto, *l.c.*); the *benzenesulphonic derivative* $SO_2Ph\cdot NH\cdot CHMe\cdot CO_2H$ has m.p. 126° (Hedin, Ber. 1890, 23, 3197); the *β-naphthalenesulphonic derivative* $C_{13}H_{14}O_3NS$ melts and decomposes at 220° (Koenigs and Mylo, Ber. 1908, 41, 4427); for *hippurylalanine* $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 202°, and derivatives, see Curtius and Lambotte, J. pr. Chem. 1904, [2] 70, 109); *phthalylalanine* $C_6H_4:(CO)_2:N\cdot CHMe\cdot CO_2H$, m.p. 164°, and *phthaloylalanine* $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, H_2O, m.p. 129° (Andreasch, Monatsh. 1904, 25, 774); *palmityl-α-alanine* $CH_3(CH_2)_{14}\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 110°, $[\alpha]_D^{10°}$ − 5·98° (Abderhalden and Funk, Zeitsch. physiol. Chem. 1910, 65, 61); *diethyldialaninquinone* $C_6H_2O_2(NH\cdot CHMe\cdot CO_2Et)_2$ forms red prisms, m.p. 140° (corr.) (Fischer and Schrader, Ber. 1910, 43, 525); 2:4-*dinitrophenyl-dl-alanine*, m.p. 178° (Abderhalden and Blumberg, Zeitsch. physiol. Chem. 1910, 65, 318).

Among the polypeptides prepared by Fischer, Abderhalden, and others, there are many containing the 'alanyl' group one or more times, *e.g. r-alanylalanine* $NH_2\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 276° (corr.), the *benzoyl derivative* m.p. 203°–204°, the *ethyl ester* m.p. 114°–116°; *dialanylalanine* $NH\cdot[CHMe\cdot CO\cdot NH]_2\cdot CHMe\cdot CO_2H$, m.p. 219° (corr.) (Fischer and Kautzsch, Ber. 1905, 38, 2375); *l-alanyl-d-alanine*, m.p. 269°–270° (corr.), $[\alpha]_D^{20°}$ − 68·5°; *d-alanyl-l-alanine*, m.p. 275°–276° (corr.), $[\alpha]_D^{20°}$ +68·94° (Fischer and Raske, Ber. 1906, 39, 2893, 3981), and the tetrapeptide *glycyl-tyrosyl-glycyl-d-alanine* decomposing at 225° (corr.) is probably a mixture of stereoisomerides of the tetrapeptide isolated from silk fibroin (Fischer, Ber. 1908, 41, 2860; *cf.* Abderhalden and Hirszowski, Ber. 1908, 41, 2840). For other polypeptides derived from alanine, see Fischer (Ber. 37, 2486; 4585; 38, 2375; 2914; Annalen, 340, 128, 152; Ber. 39, 453; 40, 943, 1754, 3717; Annalen, 363, 136), and Abderhalden (Ber. 41, 2840; 2857; 42, 3394; Zeitsch. physiol. Chem. 63, 401; 65, 417).

β-Alanine, *β-aminopropionic acid* $H_2N\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by treating β-iodopropionic acid with ammonia (Mulder, Ber. 9, 1902) or with silver nitrite and reducing the resulting *nitro-* compound with tin and hydrochloric acid (Lewkowitsch, J. pr. Chem. [2] 20, 159); by heating ethyl acrylate with alcoholic ammonia in sealed tubes at 110° (Wender, Gazz. chim. ital. 19, 437); or by the action of potassium hypobromite on an alkaline solution of succinimide—this is the best method, and gives a yield of 60 p.c. of the theoretical (Hoogewerf and van Dorp, Rec. trav. chim. 10, 4; Holm, Arch. Pharm. 242, 590).

β-Alanine forms prisms m.p. 196° (Hoogewerf and van Dorp, *l.c.*), does not melt at 220° (Kursda, Monatsh. 12, 422), m.p. 206°–207° (Lengfeld and Stieglitz, Amer. Chem. J. 15, 504); the hydrochloride of the *methyl ester* has m.p. 94°–95° and of the *ethyl ester* m.p. 65·5°. The *copper salt* $Cu(C_3H_6NO_2)_2,6H_2O$ has the properties of an ordinary copper salt, and not those of a cuprammonium derivative (Callegari, Gazz. chim. ital. 1906, 36, ii. 63).

β-Alanine does not occur naturally in the body; when administered with food it causes an increase in the urinary nitrogen, but it is apparently changed with more difficulty than α-alanine, as the increased nitrogen excretion is not observed until the second day (Abderhalden and Schittenhelm, Zeitsch. physiol. Chem. 1907, 51, 323). M. A. W.

ALANT CAMPHOR *v.* CAMPHOR.

ALANT ROOT. The root of *Inula helenium* is said to contain antiseptic principles, efficacious against tuberculosis bacilli. By distilling the root with water, *helenin*, *alantic acid*, and *alantol* (alant camphor) are obtained. *Alantic acid* $C_{15}H_{22}O_3$ crystallises from alcohol in white crystals, m.p. 91°; and on heating it forms the *anhydride* $C_{15}H_{20}O_2$. Both acid and anhydride are insol. in water, sol. in alcohol or fatty oils; form sol. salts with alkalis. *Alantol* is an aromatic liquid, b.p. 200° (Marpmann, Pharm. Zent. 8, 122; J. Soc. Chem. Ind. 1887, 520).

ALBERTITE. A jet-black mineral substance resembling asphalt, discovered in 1849, at Hillsborough, Albert co., New Brunswick. Used in the United States for the production of oil and coke. The yield per ton is said to be 100 gallons of crude oil, and 14,500 cubic feet of illuminating gas, whilst a residue of good coke remains in the retorts. Albertite has been found at Strathpeffer, Ross-shire; it contains 62 p.c. volatile matter, 37 p.c. fixed carbon, and 0·60 p.c. water. Its ultimate composition is 79·75 p.c. carbon, 8·12 p.c. hydrogen, 1·63 nitrogen, and 10·30 oxygen (Morrison, Min. Mag. 6, 101; Chem. Soc. Abstr. 50, 311).

ALBITE *v.* FELSPAR.

ALBUM GRÆCUM. A term formerly used for the excrement of dogs. It was at one time supposed to have medicinal properties, but is now used only for tanning, as skins treated with it, after the removal of the hair and previous to tanning, preserve their softness. It consists mainly of phosphate of lime. Fowls' dung is said by tanners to answer the purpose better.

ALBUMINOIDS and ALBUMINS *v.* PROTEINS.

ALCOHOL (Ethylic or Vinous), the active principle of intoxicating liquors, is, in the dehydrated condition, a colourless liquid, having a specific gravity of 0·791 at 20°/20° (Lowitz, Crell's Ann. 1796, 1, 1), 0·7938 at 15·6°/15·6° (Fownes, Phil. Trans. 1847, 249), 0·793811 at 15·6°/15·6° (Drinkwater, Phil. Mag. Feby. 1848), 0·79350 at 15·6°/15·6°, 0·79367 at 15°/4° (Mendeléeff, Pogg. 138, 230), (Squibb, Ephemeris, 1884–5, and Pharm. J. [3] 16, 147–148). It boils at 78·4° under a pressure of 760 mm. (Kopp, Annalen. 92, 9), and solidifies at −130·5° (Wroblewski and Olsewski, Compt. rend. 96, 1140 and 1225). It is inflammable, the combustion evolving great heat but little light, and producing carbon dioxide and water. It acts as a caustic irritant in contact with the tissues of the body, owing probably to the energy with which it draws moisture from the surface. It possesses a specific heat of 0·6120, at temperatures between 16° and 40·5° (Schüller, P. Erg. 5, 116–192). Its index of refraction for $H\beta$=1·3667 (Brühl), and its critical temperature 234·6° at 48·9 m. At this point 1 gram occupies 3·5 c.c. (Ramsay and Young, Proc. Roy. Soc. 38, 329).

Alcohol forms ethoxides with sodium and potassium, and unstable compounds with certain crystalline salts, *e.g.* zinc chloride, the latter called alcoholates. Subjected to the action of a limited supply of oxygen, it is converted into aldehyde (C_2H_4O), which, by further oxidation, becomes acetic acid ($C_2H_4O_2$). Distilled with chloride of lime, it forms chloroform ($CHCl_3$). With sulphuric acid at a temperature not exceeding 145° it yields ether ($C_4H_{10}O$). With twice its bulk of sulphuric acid it gives ethylene (C_2H_4). With excess of dry chlorine gas it produces chloral (C_2HCl_3O).

Preparation.—Synthetically from its elements thus:—By passing an electric arc between carbon poles in an atmosphere of hydrogen, acetylene (C_2H_2) is produced, which, in the presence of nascent hydrogen, becomes ethylene (C_2H_4). Ethylene by protracted shaking with sulphuric acid is converted into sulphovinic acid, which, being distilled in presence of water, produces alcohol.

Alcohol is, for practical purposes, prepared by dehydrating the products of the distillation of fermented liquids. Up to 1796 the strongest spirit known contained not less than 5 p.c. of water. Lowitz appears to have been the first to prepare it in an approximately anhydrous condition. His process consisted in first increasing the strength of rectified spirit by adding to it dry potassium tartrate, and after decanting from this, distilling very slowly in presence of great excess of dry potassium carbonate. Richter used, instead of potassium carbonate, hot calcium chloride (Crell's Ann. 2, 211). Drinkwater first digested with dry potassium carbonate for twenty-four hours; decanted the strong spirit thus produced, digested with as much fresh-burnt quicklime as was sufficient to absorb the whole of the alcohol, and afterwards distilled in a water-bath at a temperature of 82·2°. The product of this distillation, which was found to have a specific gravity of 0·7946 at 15·6°, was returned to the retort, and a fresh quantity of dry pulverised quicklime added to it, after which it was allowed to digest for a week at a temperature of 15·6°. It was then again slowly distilled and the specific gravity of the product found to be 0·7944 at 15·6°. This was digested at a temperature of 54·4° with hot quicklime, and distilled out of contact with the air at a temperature of 81·1° to 82·2°, and the specific gravity of the product, which was taken as absolute alcohol, found to be 0·793811 at 15·6°/15·6°.

Squibb followed the process of Drinkwater, distilling in a partial vacuum of 380 to 630 mm. The alcohol thus prepared had a specific gravity of 0·79350. The difference between this specific gravity and that found by Drinkwater represents one-tenth p.c. of alcohol. Mendeléeff's observations (Pogg. 138, 103, 230) practically confirm those of Drinkwater and Fownes.[1]

Analytical Methods.—We are dependent upon specific gravity for the exact quantitative estimation of alcohol, and perhaps no method could be devised so easy of application (*v.* ALCOHOLOMETRY). It is, however, open to the objection that it assumes water to be the only volatile substance with which the spirit is mixed, aldehyde, fusel oil, and ether when existing as impurities being reckoned as alcohol. On the other hand, no chemical method, capable of practical application, has yet been devised for the exact quantitative estimation. Berthelot's process (Compt. rend. 80, 1039) of measuring the ethylene

[1] Absolutely anhydrous alcohol produces no blue colouration with dehydrated (white) copper sulphate. It should give no cloudiness when mixed with benzene. Absolutely anhydrous alcohol added to a mixture of anthraquinone (0·001 gr.) with a little sodium amalgam gives a green colouration; if a trace of water be present the colour becomes red (Claus, Ber. 10, 927).

produced by sulphuric acid and absorbed by bromine from a given quantity of spirit is a valuable qualitative test, and within limits most useful when applied quantitatively in presence of methylic alcohol. The production of iodoform (Hager, Compt. rend. 82, 768) may be employed with advantage as a preliminary test for small quantities of alcohol, but as other bodies produce iodoform in the same circumstances, it cannot be regarded as conclusive. For the detection of alcohol in ether, Allen (Chem. Soc. Trans. 1877, 2, 930) suggests that a little fuchsine be shaken up with water and ether, and 10 c.c. of the solution thus formed agitated with the same quantity of the ether submitted for examination; the intensity of the colour produced would be a measure of the quantity of alcohol present. For the detection of fusel oil in alcohol, Jorissen (Bied. Zentr. 1881, 791) recommends that 10 c.c. of the spirit should be mixed with 10 drops of colourless aniline and 2 or 3 drops of sulphuric acid. A deep-red colour is formed if fusel oil be present, due to the action of furfuraldehyde, an invariable constituent of fusel oil.

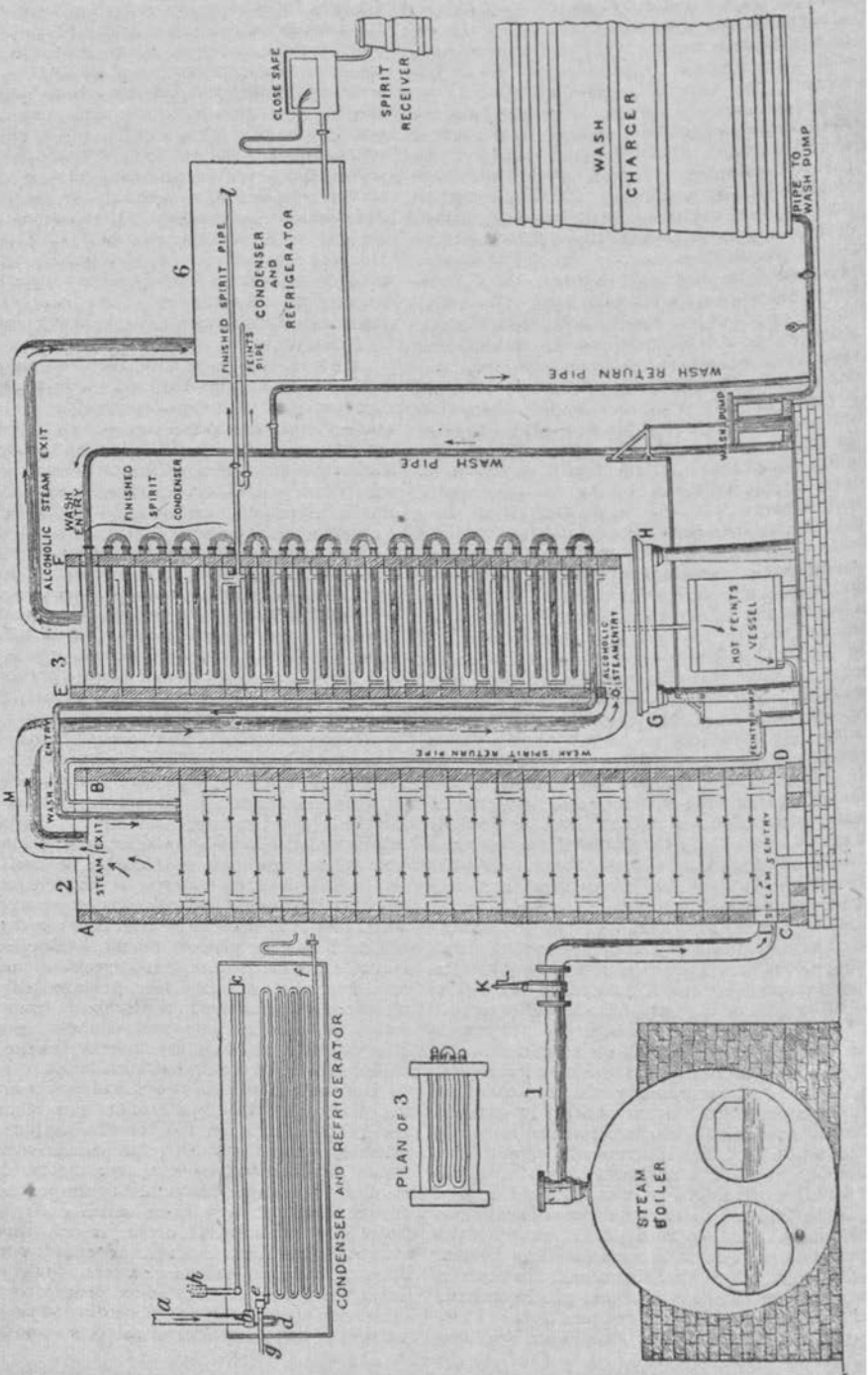
Alcohol is sometimes used as an adulterant in essential oils. A very ready test is to place a little of the oil in a dry test-tube, taking care in pouring it in that none adheres to the side. Rub a little fuchsine on the upper inside surface of the test-tube and apply heat, the presence of alcohol will be indicated by red stains in the fuchsine. No satisfactory method has yet been suggested for the estimation of aldehyde in alcohol, but the peculiar suffocating odour which accompanies it, and the brown colour produced by alkalis in the spirit, are indicative of its presence. A colorimetric method of estimation is generally employed by comparison of the sample with a standard solution of aldehyde, using Schiff's reagent.

Manufacture.—The first process in the manufacture of spirit is one of brewing, and in general principles it does not differ from that employed in making beer. The brewer, as well as the distiller, endeavours to treat his materials in such a way as to extract from them the greatest amount of fermentable matters. The brewer of beer, however, does not desire to convert all the matter he extracts into spirit, and he brews at such gravities as his customers require. The distiller desires to convert as much as possible of the matter he has extracted from his materials into spirit; he therefore produces a wort containing more maltose and less dextrinous matter than the brewer of beer. He has also an advantage over the brewer in being able to choose the gravities which he knows by experience will produce the best results. It has been found that for distillers' purposes it is advisable to keep the specific gravity of the wort when set for fermentation below 1040. The principle of low temperatures when the diastase is acting in the mash tun appears to be fully recognised, 60° to 63° being generally adopted, and it is understood that the higher the temperature at which the worts are set for fermentation, the greater is the amount of fusel oil in the spirit. The distiller has, therefore, to choose the lowest temperature at which a healthy fermentation can be started, and this is found to range between 23° and 25°. He cannot be too careful as to the purity of the yeast, for not only has he to run the risk of acetic and other ferments being introduced into the wort, involving loss of alcohol, but to provide against the presence of aldehyde, which is objectionable in the spirit. Kekulé attributes the presence of aldehyde to the action of nitrates derived from the materials. It is found in practice that it is always more prone to appear in hot weather, when the difficulty of keeping the yeast from decomposition is greatest, and as yeast always contains some spirit in a dilute form it is not improbable that the aldehyde is frequently a product of the oxidation of this spirit.

The materials used in the manufacture of alcohol in the United Kingdom are chiefly malt, maize, rice, sago, tapioca, barley, rye, oats, sugar, and molasses, but occasionally dates and locust beans have been employed. At the present time *maize* constitutes fully 75 p.c. of the grain used. In Scotland the smaller distillers use malt only, and the spirit they produce under the name of Highland, Campbeltown, or Islay Whiskey, Glenlivet, Lochnagar, &c., has imparted to it a flavour derived partly from the peat used in drying the malt. The process of manufacture consists in distilling the fermented wort—then called wash—in a common still, collecting the distillate, which is weak spirit contaminated with fusel oil, and is called 'low wines,' and redistilling. The spirit which passes over in the middle of the redistillation is that which is used for consumption. It contains from 60·8 to 76·7 p.c. of alcohol by weight (20 overproof to 45 overproof), but is generally diluted by the addition of water to 55·4 p.c. of alcohol by weight (11 overproof) before being sent into consumption or placed in bond. Irish whiskey differs from Scotch chiefly in the absence of peat flavour. The materials used in its manufacture are, with one or two exceptions, a mixture of malt and grain, the proportion of malt being, however, greater than in English distilleries. It is generally bonded at 25 overproof (64 p.c. of alcohol by weight).

We have hitherto dealt with the spirit manufactured in 'Common' or 'Pot' stills, or in other words by boiling the wash, condensing the steam thus produced, reboiling the product and recondensing. But by far the greater quantity of the alcohol of commerce is produced by the Coffey still, in which the alcoholic vapour produced is deprived of water as the process continues until a spirit is formed of much greater purity than that manufactured by the old method. The annexed illustration represents a Coffey's distilling apparatus, the left-hand column being called the *analyser*, the right hand one the *rectifier*. The first operation is to fill both columns with steam. This is accomplished by introducing it under pressure from the boiler at C, whence it ascends within the analyser, passing by the pipe M into the bottom of the rectifier. When a proper temperature has been attained, the wash is pumped from the wash charger by a pipe which enters the top of the rectifier. This pipe is only shown sectionally in the sketch after entering the column, but it is continuous, and the wash passes slowly through it, becoming warmer, owing to the pipe being in contact with the steam. When it has reached the bottom of the

rectifier it is not far from the boiling-point. It will be seen that the pipe then ascends, and finally delivers the wash into the top of the analyser. The lines across the analyser represent plates of perforated copper, and in connection with each is a tube which projects about an inch and a half above the plate, and dips into a shallow vessel placed on that next beneath. The wash on entering falls on the first plate, but on reaching a depth of an inch and a half passes through the tube to the second one. In the mean time the steam produces ebullition in the contents of the plates, and carries away with it the alcoholic vapour through the steam exit



pipe, so that by the time the wash has reached the bottom of the column it has been deprived of its alcohol. The alcoholic vapour passes by the pipe M into the bottom of the rectifier, which like the analyser contains plates and metal tubes, and where a process of gradual cooling takes place by the action of the pipe carrying the cold wash. Fusel oil vapour, condensing at a higher temperature than alcohol, is the first to assume the liquid form, and contaminated with spirit passes into the hot 'feints' receiver. The vapour containing alcohol continues to ascend, meeting with portions that have condensed, and are undergoing the process of rectification. It will be seen that the upper part of the apparatus is marked off in the sketch as finished-spirit condenser. It is so called because all that condenses within its area, instead of returning towards the bottom of the apparatus to be rectified, passes by the finished-spirit pipe or feints pipe into the receivers. At the top of the apparatus is a pipe marked 'alcoholic steam exit,' which carries away most of the aldehyde as well as spirit vapour which under special circumstances may not have been condensed before reaching that point.

The English distillers confine themselves almost exclusively to this apparatus, brewing for the most part from a mixture of grain and malt. In addition to Coffey's still, various forms of rectifying stills are in use to meet special requirements, *e.g.* the production of a purer though not stronger spirit than that obtainable from the Coffey still for the purpose of compounders and certain manufacturing processes, and apparatus having for their object (in consequence of the increasing demand for fusel oil) the recovery of the maximum amount of this by-product, which indeed is now considerably more valuable than the spirit itself. The spirit produced does not to any large extent go into consumption as whiskey, the want of flavour being an objection in regard to the better qualities. Large quantities are transferred to the rectifiers, who redistil them with various flavouring ingredients, producing gin, British brandy, British rum, and the various cordials. A portion, after being redistilled from potash or potassium carbonate, or filtered through charcoal, is used in the arts and in medicine under the names of rectified spirit and spirits of wine. The British Pharmacopœia (1898) requires rectified spirit to be of a specific gravity of 0·834, equal to 85·65 p.c. of alcohol by weight. The Pharmacopœia of the United States fixes it at 0·820, equal to 91 p.c., which is about the strength it comes from Coffey's apparatus. It is from this spirit that anhydrous or absolute alcohol is generally prepared. It varies considerably in flavour, and, according to the United States Dispensatory, 1883, the purest is produced under Atwood's patent, in which permanganic acid is used to destroy the disagreeable organic substances. It has been suggested that the purity of strong spirit might be considerably increased by redistilling *in vacuo*. Reference has already been made to the occurrence in variable quantity of secondary products on fermentation. Pasteur (Ann. Chim. Phys. 58, 330) showed that on the fermentation of sugar 3·16 p.c. of glycerol and 0·67 p.c. of succinic acid are produced. These bodies are, however, very slightly volatile, and therefore can only pass into the spirit in very small proportion.

We have hitherto only dealt with spirits manufactured in the United Kingdom. Of the more important foreign spirits, the principal is brandy, the production of which from grape wine is an industry confined almost entirely to France. The best brandy is derived from white wine, but a considerable quantity of spirit is imported from the Continent under the name of brandy, which has either been mixed with other spirits or prepared from substances bearing no relation to wine. The distillation of genuine brandy takes place in stills which are practically on the pattern of common or pot stills; the improvements being chiefly confined to the adoption of means for carrying on the distillations continuously. Illustrations of the various stills now in use, will be found in Duplais' treatise on the manufacture and distillation of alcohol. Brandy is generally imported into this country at a strength a little below proof (47 to 48 p.c. of alcohol by weight) (*v.* BRANDY).

Rum is the spirit produced by fermenting diluted molasses and distilling the product in an ordinary still. Its character is due to the formation of ethyl butyrate, which, when added to other spirits, produces a flavour difficult to distinguish from genuine rum. The strength at which rum is generally imported into this country is about 35 overproof (70 p.c. of alcohol by weight) (*v.* RUM).

The molasses from the beet-sugar manufactories in France is now utilised in making spirit, being simply neutralised, generally mixed with a little rye flour and malt, fermented and distilled. The best qualities of spirits thus produced are devoid of taste or any peculiar aroma, and are employed in the manufacture of liqueurs, for improving common brandies, and for refining rectified spirit.

Geneva or *Hollands* is a well-known form of gin manufactured in Holland, where the grain spirit is for the most part made from a mixture of malt and rye. It does not possess any characteristic to distinguish it from the same article manufactured by rectifiers in this country, and its consumption appears to be declining (*v.* GIN). Absinth is a form of gin in which the spirit is flavoured with the bitter principle of wormwood, together with extracts of some or all of the following plants: fennel, hyssop, anise coriander, angelica seed, dried veronica, chamomile, and mint (*v.* ABSINTH). A large quantity of spirit manufactured in Germany from potatoes is imported into this country, coming into competition with the lowest qualities of spirits of wine of the British distilleries.

Reference has already been made to the bonding of whiskey—that is, placing it in warehouses under the control of the revenue authorities, where it remains maturing for periods varying from a few months to several years. The exact change which takes place during the maturing process has not yet been satisfactorily explained, although the labours of Pelletan, Dumas and Stas, Gaultier, Chancel, Wurtz, Cahours, Balard, Liebig and Pelouze, Pasteur, Fittig, and Krämer and Pinner have added largely to our knowledge of the subject. According to the researches of these authorities fusel oil is a complex

substance and a necessary accompaniment to fermentation. In grain fermentations amyl alcohol is the predominant constituent of this oil, but propyl and butyl alcohol are also present. In wine fermentations it consists principally of œnanthyl and caproyl alcohols. It is probable that these alcohols are converted, in the process of maturing the spirit, from a disagreeable-smelling and highly intoxicating body into compound ethers which are both fragrant and harmless.

In the process of mellowing there is generally a loss of alcohol, varying with the length of time and the condition of the atmosphere of the warehouse. The revenue authorities fully recognise this, and make the necessary allowances in charging the duty. It will therefore be apparent that alcoholic strength based on specific gravity is not always a measure of the money value of spirits as beverages. The Food and Drugs Amendment Act (42 & 43 Vict. c. 30) has fixed a limit below which spirits shall be assumed to be diluted. This limit is 25 under proof (35·8 p.c. of alcohol by weight) for whiskey, brandy, and rum; and 35 under proof (30·8 p.c. alcohol by weight) for gin.

Uses.—In addition to its use as a beverage, spirit is employed as a solvent for many of the drugs required in medicine, and diluted to the standard of British proof—that is, to the specific gravity of 0·91984 at 15·6°, representing 49·24 p.c. by weight of Drinkwater and Fownes alcohol—it forms part of a large proportion of the tinctures of the Materia Medica. It is also used largely as a solvent for essential oils, in preparing perfumes and essences, and ether is manufactured from it. The alcohol used in all the above preparations pays a duty of 15*s.* 1*d.* per proof gallon, equal to about 27*s.* per gallon of the alcohol of Gay-Lussac, the standard of France.

Adulteration.—Although it has been stated that spirits, especially gin, were formerly adulterated with capsicum and even sulphuric acid, in order to increase their fiery character, it is satisfactory to find that in the working of the Food and Drugs Act no evidence has been afforded of such practices during late years. The report of the Local Government Board (1909) shows that the adulterants detected during the year consisted of water (the great majority of cases); foreign spirit in 16 samples out of 5217 samples of brandy, rum, and whiskey examined; one case (whiskey) contained an admixture of sherry wine.

Methylated spirit. In 1853 a strong representation was made to the Government to allow the use of alcohol duty free in the arts and manufacturing processes in which it was required, and after careful inquiry the Board of Inland Revenue in 1855 decided to sanction, under certain restrictions, a mixture of nine parts of spirits of wine and one part of methyl alcohol (wood naphtha) free of duty under the name of *methylated spirits*. In 1861 the permission was extended to all other purposes except consumption as a beverage or as a medicine. The reasons for selecting wood naphtha were that whilst it would be least likely to interfere in any of the processes for which alcohol was required—especially as a solvent—it would be very difficult to separate from the alcohol when once mixed. The principal restriction on the use of methylated spirit is that it shall only be kept by authorised persons and in authorised premises.

In 1891 it was found necessary (owing to the possibility of methylated spirit being sufficiently purified to render it fit for potable purposes, and the growing practice of drinking even the unpurified methylated spirit by the poorer classes in some of the larger cities) to again restrict the use of methylated spirit made as above described (*i.e.* 'ordinary methylated spirit') to manufacturers only, and, even then, subject to revenue restrictions, and to prescribe the addition of a further denaturant to methylated spirit intended for general purposes. This denaturant consists of mineral naphtha (petroleum), and the mixture, known as '*mineralised*' methylated spirit, may be sold by licensed retailers to the general public for any purpose to which it is applicable, as lighting, heating, cleansing, or mixing with paints, varnishes, &c.

It was found, however, that 'ordinary' methylated spirit was not universally applicable to manufacturing processes requiring the use of alcohol, and accordingly, in 1902, the Commissioners of Inland Revenue, under powers conferred upon them by the Spirits Act of 1880 and the Finance Act of 1902, authorised the use of duty-free alcohol denatured with substances other than wood-naphtha in certain manufacturing operations and subject to special conditions.

As the result of an inquiry by a Departmental Committee, in 1904–5, the amount of wood-naphtha to be used as a denaturant for 'ordinary' methylated spirit used for industrial purposes was reduced from 10 to 5 p.c. of the mixture. This is described as '*industrial*' *methylated spirit.*

At the present time (1911), there are, therefore, two descriptions of methylated spirit officially recognised in the United Kingdom, viz.:

(*a*) *Mineralised methylated spirit* as sold by licensed retailers for general use (except for the preparation of beverages or medicine), and containing not less than 10 p.c. by volume of approved wood-naphtha, and, in addition, not less than 0·385 p.c. of approved mineral naphtha (petroleum of specific gravity not less than 0·800).

(*b*) *Industrial methylated spirit*, intended for use in manufacturing processes, and sold only by methylators to persons authorised to receive this kind of spirit. This must contain not less than 5 p.c. of approved wood-naphtha or other substance or combination of substances approved by the Commissioners of Customs and Excise.

The wood-naphtha must be sufficiently impure to make the methylated spirits so nauseous as to render them incapable of being used as a beverage or of being mixed with potable spirits without rendering them unfit for human consumption. It must contain not less than 72 p.c. by volume of methyl alcohol, and not more than 12 grams per 100 c.c. of aldehydes, acetone, and higher ketones, estimated as acetone by Messinger's iodoform process, nor more than 3 grams of esters estimated as methyl acetate by hydrolysis; not more than 30 c.c. of naphtha shall be required to decolourise an aqueous solution containing 0·5 gram of bromine, and 5 c.c. at least of deci-normal acid shall be required to neutralise 25 c.c. of the spirit when methyl orange is used as indicator.

The wood-naphtha which is now used by methylators is fairly uniform in character as regards its content of methyl alcohol, and it is by the recognition of this alcohol that the presence of methylated spirits is usually detected. Acetone is present in much more varying quantities, whilst unsaturated alcohols, compound ethers, and nitrogenous basic substances are present in too small and varying proportions to afford suitable means for dectecting methylated spirits in mixtures.

The most satisfactory methods for detecting methyl alcohol in presence of ethyl alcohol depend either on differences in the physical properties of the alcohols themselves, or on differences in the chemical behaviour of their derivatives or products of oxidation, but of these, few are capable of indicating with certainty the presence of less than 1 p.c. of methyl alcohol.

Of the methods which have hitherto been devised for this purpose, none can compare, as regards the certainty of the conclusions which may be drawn from the results, with that of Riche and Bardy, which depends on the ultimate formation of methylaniline violet and its deposition on merino-wool (Compt. rend. 1875, 1076). As a preliminary test, and one which may with advantage be incorporated in the Riche and Bardy process, the following will be found to be useful. About 10 c.c. of the strong spirit—freed, if necessary, from essential oils, &c., by the salt-petroleum method and fractionated from potassium carbonate (*v.* ALCOHOLMETRY)—are placed with 30 grams of powdered iodine in a small round-bottomed flask which can be readily connected with a condenser. Two grams of amorphous phosphorus are added and the resulting alkyl iodides distilled and collected under water in a small separator. When from 10 to 12 c.c. have been collected, the iodides are washed with water, decolourised with dilute potash, and drawn off from the aqueous layer into a flask containing a little freshly heated potassium carbonate. After remaining an hour or so with occasional shaking, the potassium carbonate is removed by filtration, and the boiling-point of the iodides carefully determined. Ordinary ethyl alcohol yields an iodide which has a constant boiling-point of 72°. When methyl alcohol is present in the spirit, the initial boiling-point of the iodides is lower and a portion distils below this temperature. By noting the temperature at which the first drop of distilled iodides falls into the condenser and receiver respectively, the presence of relatively small quantities of methyl alcohol can be detected. The results (see table in next col.) obtained with synthetic mixtures indicate the delicacy of the method.

In doubtful cases, or when the initial boiling-point is below 70°, the first fraction of 3 c.c. of distilled iodides is digested with an equal volume of aniline at a moderate temperature, and the Riche and Bardy method proceeded with. After standing one hour, hot water is added to the crystalline mass, and the mixture boiled for some minutes, 25 c.c. of strong potash solution are then added, and the liberated aniline oil washed with water; 1 c.c. of this oil is intimately mixed with 10 grams of a mixture consisting of 100 grams of dry quartz sand, 3 grams of cupric nitrate, and 2 grams of common salt, and the mixture introduced into a wide tube and heated for some hours at 90°–100°. The product is exhausted with warm alcohol and the extract filtered and made up to a volume of 100 c.c.

If the sample of spirit contained ethyl alcohol only, the colour of the liquid will be red, but in the presence of 1 p.c. of methyl alcohol it has a distinct violet shade, whilst in the presence of 2 p.c. the violet is very decided, and becomes more so as the proportion of methyl alcohol increases. 5 c.c. of the alcoholic extract are then mixed with water to a volume of 100 c.c., and 2 c.c. of this dye diluted with water to about 400 c.c. The mixture is now heated to a temperature not exceeding 75°, and from two to three feet of Berlin wool, previously freed from grease by treatment with hot dilute potash, immersed in it for 30 minutes. Pure ethyl alcohol under these conditions will not produce a dye, and the wool after washing and drying remains practically white. If, however, methyl alcohol was originally present, the fibre will be violet, the tint becoming more intense and increasing in depth according to the quantity present. Riche and Bardy recommend that 5 c.c. of the above diluted dye should be taken instead of 2 c.c. as here described, but although by this means a more intense dye is obtained when methyl alcohol is present, it is found that an appreciable dye, although not of the same colour, is deposited when pure ethyl alcohol has been operated with, and this may lead to confusion. For purposes of comparison it is therefore advisable to operate concurrently with a sample of rectified spirits.

Percentage of methyl alcohol by volume in the mixture of alcohols	Temperature at which the first drop of iodides falls into the condenser	Volume of distillate obtained below 72° from 10 c.c. of iodides
		c.c.
Nil	70°	Nil
0·38	69°	0·2
0·94	65°	0·8
1·86	63°	2·2
2·77	62°	4·0
3·66	60°	5·0
4·55	58°	6·0
5·42	57°	6·2
6·26	56°	6·4
7·10	55°	6·5
10·00	52°	7·5

If it be desired to estimate the proportion of methyl alcohol or methylated spirits in a sample, the method of Thorpe and Holmes may be employed. This method depends on the complete oxidation of methyl alcohol to carbon dioxide by means of chromic acid mixture, rectified spirits under the same conditions yielding only a small quantity of carbon dioxide equivalent to 0·01 gram for each gram of ethyl alcohol present (Chem. Soc. Trans. 1904, 1).

As a result of many experiments it has been proved that unless the boiling-point of the iodides is abnormal, no dye is obtained by the Riche and Bardy method, nor does the yield of carbon dioxide on oxidation exceed the limits

given above for rectified spirits, but in all cases in which a dye is obtained a proportional excess of carbon dioxide is also obtained.

In other countries there are, as a rule, classes of denatured alcohol corresponding more or less with those authorised in the United Kingdom, *i.e.* spirit for general use so completely denatured as to be deemed undrinkable, and spirit not absolutely denatured and intended for use by responsible manufacturers subject to a more or less strict revenue control.

Wood-naphtha is the denaturant most in favour for spirit intended for general use, the nauseous character of the methylated spirit being sometimes intensified by the addition of such substances as pyridine bases, benzine, &c.

In *France*, spirit for general use contains one-eleventh of its volume of officially approved wood-naphtha, with an addition (when used for lighting and heating purposes) of 0·5 p.c. of heavy benzine distilling between 150° and 200° and 4 p.c. of gum resin for 'finish.'

In *Germany*, the official formula is 2 p.c. of wood naphtha, 0·5 p.c. of pyridine bases, and (optionally) 0·125 p.c. of rosemary oil. Spirit intended for motor cars, and internal combustion engines is denatured by adding 1 p.c. of wood-naphtha, 0·25 p.c. of pyridine bases, 0·25 p.c. of a solution of methyl violet dye, and from 2 to 20 p.c. of benzol to the pure spirit.

In the *United States of America*, 10 p.c. of approved methyl alcohol and 0·5 p.c. of benzene is prescribed to be added to spirit denatured for general use.

Austrio-Hungary: Two p.c. of wood-naphtha, 0·5 p.c. of pyridine bases, and a trace of phenol phthalein are added to spirit intended for general purposes.

In *Belgium* and *Russia* specific denaturants are prescribed for each of the principal manufacturers, and this practice obtains in certain other countries, as Germany, France, Switzerland, and the United Kingdom, when it can be shown that ordinary methylated spirit is unsuitable. In such cases the denaturants are naturally very varied in character, being specially adapted to the particular necessities of each manufacturer.

(Minutes of Evidence and Report of the Departmental Committee on Industrial Alcohol, 1905; Herrick, Denatured or Industrial Alcohol.)

ALCOHOLOMETRY is the term applied to any process for estimating the amount of alcohol in a spirituous liquid. In simple mixtures of alcohol and water a determination of specific gravity at a standard temperature affords an accurate index of alcoholic content, and it is by taking advantage of this fact that the assay of spirit for revenue and commercial purposes is usually carried out.

When alcohol and water are mixed together the volume of the mixture is invariably less than the sum of the initial volumes, and the degree of contraction varies with the proportion of alcohol present. In countries in which the revenue from spirit is of great importance it has therefore been found necessary to ascertain by experiment the specific gravities of mixtures of alcohol and water in all proportions and at various temperatures. These experiments have in general been carried out at the request of the Governments interested, and the results are embodied in tables associated with the names of those entrusted with the investigations.

In 1794 Sir Charles Blagden and Mr. Gilpin completed an extensive series of experiments, undertaken at the request of the British Government (Phil. Trans. 1790–1794), the results of which have since served as the basis of systems of alcoholometry in this and other countries. At that time anhydrous alcohol had not been prepared, Blagden and Gilpin's tables having reference to spirit of a sp. gr. 0·825 at 15·6°/15·6° (60°/60°F.). Tralles, in 1811, conducted a like investigation for the Prussian Government (Gilb. Ann. 1811), and adopted 0·7946 as the specific gravity of alcohol at 15·6°/15·6°. He incidentally confirmed the general accuracy of the results of Blagden and Gilpin, and constructed tables of spirit-strengths which for upwards of sixty years formed the basis of German alcoholometry. Similar researches were undertaken by Gay-Lussac (Paris, 1824), McCulloch (Washington, 1848), Baumhauer (Amsterdam, 1860), Mendeléeff (St. Petersburg, 1865), and more recently by the Kaiserliche Normal Eichungs Kommission (Berlin, 1889), the several results of which have from time to time been incorporated in the systems of alcoholometry adopted by the respective Governments. The unofficial investigations of Fownes (Phil. Trans. 1847), Drinkwater (Chem. Soc. Mem. 1848), and Squibb (Ephemeris, 1884), are likewise entitled to consideration.

Drinkwater prepared alcohol of a specific gravity 0·79381 at 15·6°/15·6° (in air), whilst Squibb obtained it as low as 0·7935, but this result lacks confirmation.

The work of Mendeléeff for the Russian Government admittedly constitutes the most comprehensive and exact of the researches hitherto made in the field of alcoholometry. Mendeléeff obtained alcohol of a specific gravity 0·79425 at 15°/15°, which at 15·6°/15·6° is equivalent to 0·79384 in a vacuum, or to 0·79359 in air, and he assigned to Drinkwater's alcohol an alcoholic content of 99·95 p.c., and to the strong spirit of Blagden and Gilpin 89·06 p.c. by weight. The results of Tralles' and Gay-Lussac's experiments, being based on alcohol less dehydrated than that of Drinkwater, compare less favourably with those of Mendeléeff.

Mendeléeff was so well satisfied with the work of Blagden and Gilpin, and Drinkwater, that, for spirituous mixtures of low strength, he included many of their results in his tables of spirit-densities, and after a critical investigation and subsequent verification by the Kaiserliche Normal Eichungs Kommission, his results have been substantially adopted as the basis of the present system of German alcoholometry in place of the relatively less accurate data of Tralles.

The results of the work of these four authorities have been incorporated in the accompanying table of spirit-densities, which may serve for the pyknometrical determination of the true strength of spirits. In the assessment of duty and in commercial transactions, the standard of strength is termed 'proof.' Spirit of proof strength is defined as 'that which at the temperature of 51°F. (10·6°C.) weighs exactly ⅞ths of an equal measure of distilled water' also at 10·6°. According to the best available data this mixture of alcohol and water has a specific gravity of 0·91976 at 15·6°/15·6°, and contains

Specific gravity in air at $\frac{15{\cdot}6^\circ}{15{\cdot}6^\circ}$	Percentage of alcohol		Percentage of fiscal proof spirit	Specific gravity in air at $\frac{15{\cdot}6^\circ}{15{\cdot}6^\circ}$	Percentage of alcohol		Percentage of fiscal proof spirit
	by weight	by volume at 15·6°			by weight	by volume at 15·6°	
0·79359	100·00	100·00	175·35	0·898	58·93	66·67	116·81
0·794	99·87	99·92	175·21	0·900	58·06	65·83	115·33
0·796	99·22	99·52	174·52	0·902	57·18	64·98	113·84
0·798	98·57	99·12	173·80	0·904	56·31	64·13	112·35
0·800	97·91	98·70	173·07	0·906	55·42	63·26	110·82
0·802	97·25	98·28	172·33	0·908	54·54	62·39	109·29
0·804	96·57	97·84	171·56	0·910	53·65	61·51	107·74
0·806	95·89	97·39	170·77	0·912	52·77	60·63	106·20
0·808	95·20	96·93	169·96	0·914	51·88	59·74	104·63
0·810	94·50	96·45	169·13	0·916	50·98	58·83	103·05
0·812	93·80	95·97	168·28	0·918	50·08	57·92	101·43
0·814	93·08	95·47	167·41	0·91976	49·28	57·10	100·00
0·816	92·36	94·97	166·51	0·920	49·17	56·99	99·80
0·818	91·63	94·45	165·60	0·922	48·25	56·05	98·16
0·820	90·90	93·92	164·67	0·924	47·33	55·10	96·49
0·822	90·16	93·38	163·72	0·926	46·40	54·14	94·80
0·824	89·41	92·83	162·75	0·928	45·47	53·16	93·09
0·826	88·65	92·26	161·76	0·930	44·53	52·18	91·36
0·828	87·88	91·69	160·75	0·932	43·59	51·18	89·61
0·830	87·11	91·11	159·73	0·934	42·62	50·15	87·81
0·832	86·34	90·52	158·69	0·936	41·64	49·10	85·97
0·834	85·56	89·91	157·63	0·938	40·65	48·04	84·10
0·836	84·78	98·30	156·56	0·940	39·65	46·95	82·19
0·838	83·99	88·68	155·47	0·942	38·64	45·85	80·26
0·840	83·20	88·06	154·37	0·944	37·60	44·71	78·26
0·842	82·40	87·42	153·25	0·946	36·54	43·54	76·21
0·844	81·60	86·77	152·12	0·948	35·46	42·35	74·12
0·846	80·79	86·12	150·97	0·950	34·37	41·13	71·98
0·848	79·98	85·46	149·80	0·952	33·25	39·87	69·76
0·850	79·17	84·78	148·62	0·954	32·09	38·57	67·48
0·852	78·35	84·11	147·43	0·956	30·90	37·20	65·09
0·854	77·53	83·42	146·23	0·958	29·66	35·79	62·60
0·856	76·71	82·73	145·01	0·960	28·39	34·33	60·03
0·858	75·88	82·03	143·78	0·962	27·06	32·79	57·33
0·860	75·05	81·32	142·54	0·964	25·68	31·18	54·51
0·862	74·22	80·61	141·28	0·966	24·23	29·48	51·53
0·864	73·39	79·89	140·22	0·968	22·71	27·69	48·38
0·866	72·55	79·16	138·74	0·970	21·14	25·83	45·14
0·868	71·72	78·43	137·46	0·972	19·53	23·91	41·77
0·870	70·88	77·69	136·16	0·974	17·90	21·96	38·35
0·872	70·04	76·94	134·84	0·976	16·25	19·98	34·87
0·874	69·19	76·19	133·53	0·978	14·61	18·00	31·42
0·876	68·35	75·44	132·19	0·980	12·99	16·04	27·99
0·878	67·51	74·68	130·86	0·982	11·42	14·13	24·66
0·880	66·66	73·91	129·50	0·984	9·91	12·29	21·44
0·882	65·81	73·13	128·14	0·986	8·46	10·51	18·34
0·884	64·96	72·34	126·77	0·988	7·08	8·80	15·38
0·886	64·10	71·55	125·37	0·990	5·76	7·18	12·53
0·888	63·24	70·75	123·97	0·992	4·51	5·63	9·82
0·890	62·38	69·95	122·56	0·994	3·31	4·14	7·24
0·892	61·52	69·14	121·14	0·996	2·17	2·71	4·73
0·894	60·66	68·33	119·70	0·998	1·07	1·34	2·33
0·896	59·80	67·50	118·26	1·00000	0·00	0·00	0·00

49·28 p.c. by weight and 57·10 p.c. by volume of anhydrous alcohol. Spirits which contain a greater proportion of alcohol than is contained in proof spirit are said to be of overproof strength (o.p.), and those which contain a smaller proportion are said to be of underproof strength (u.p.). Variations of temperature are deemed not to affect the fiscal strength of spirits. Spirits which are of proof strength at 10·6° are consequently deemed to be of proof strength at other temperatures, and the same applies to spirits of any other strength, provided that no change in composition has occurred. In computing the strength of a spirit mixture reference is made to the volume of proof spirit it contains, if underproof, or will produce if overproof, at the dominant temperature, which for revenue purposes in this country is fixed at 10° (50°F.). Mendeléeff's alcohol is thus found to be 75·35 overproof, or 100 volumes at 10°, when diluted

with water to proof strength, yield 175·35 volumes at that temperature.

In the table on p. 65 specific gravities of aqueous alcoholic mixtures are correlated with percentages of alcohol by weight and by volume, and fiscal proof spirit. The specific gravities are reduced to air values and represent the ratio of the weight of a given volume of spirit to the weight of the same volume of water at 15·6° under the same atmospheric conditions; they may be converted to specific gravities in vacuum by means of the expression—

$$\frac{\delta + 0{\cdot}0012}{1{\cdot}0012}$$

Although it is probable that the density of a spirituous liquid can be determined more accurately by the use of a pyknometer than by other means, in practical operations where regard must be had to convenience, it is preferable to employ one of the many hydrometers or alcoholometers, the stems of which are variously graduated to show densities, percentages of alcohol by weight or by volume, or again arbitrary indications which can be interpreted by suitable tables.

Since the year 1816, Sikes' hydrometer has been the legal instrument for ascertaining the strength of spirits for revenue purposes in Great Britain and Ireland, as well as in most of the British Colonies. It is made of brass, gilded, and consists of a hollow sphere provided at one pole with a graduated rectangular stem uniform in section, and at the other with a conical spindle terminating in an oval counterpoise to give stability to the instrument when floating in a liquid, and also to serve as an attachment for various poises. The graduated portion of the stem contains ten principal divisions, which are equal in length, and marked '0' at the upper, and '10' at the lower end, and between these points the stem is again subdivided to 2 tenths of a division. When the instrument is floating at the '0' mark in spirit at a temperature of 15·6°, it indicates a strength of 66·7 overproof, or 92·50 p.c. of alcohol, whilst the '10' mark corresponds to a strength of 58 overproof, or 86·11 p.c. of alcohol (by weight). For strengths weaker than these a series of nine poises or weights are used, numbered consecutively from 10 to 90. The poises are made of hammered brass, gilded, and can be attached by means of a slot in the poise to the spindle of the hydrometer. The series of principal divisions can thus be repeated ten times, reading from '0' to '100,' which latter indication represents distilled water. Sikes' hydrometer indications refer to readings on the stem at the surface of the liquid in which it is floating, the capillary meniscus being disregarded, and are interpreted into proof-strengths by means of tables which are arranged so as to identify a sample of spirits at any temperature between −1·1° (30°F.) and +37·8° (100°F.).

The hydrometer which is used for strong spirits beyond the range of the ordinary Sikes' instrument is known as the 'A' or 'Light hydrometer,' and tables proper to this instrument are also issued. It is made of brass, gilded, and graduated on the stem similarly to Sikes' hydrometer. When floating at the '0' mark in spirit at a temperature of 15·6°, it indicates a strength of 73·5 overproof, or 98·24 p.c. of alcohol, whilst the '10' mark corresponds to 66·7 overproof, or 92·50 p.c. of alcohol by weight, the strength proper to the '0' mark on Sikes' hydrometer.

In the United States of America Tralles' tables are legalised, and, as in England, revenue is raised with reference to a mixture of alcohol and water termed 'proof.' American proof spirit is defined as containing one-half of its volume of Tralles' alcohol at 15·6°. For Excise purposes a series of alcoholometers are employed, each having a limited range, and indicating percentages of proof spirit—'0' representing water, '100' proof spirit and '200' alcohol—and readings at temperatures other than 15·6° are corrected by means of tables to what they would be in the same spirit at that temperature. In comparing American with British proof it is necessary to remember that the American gallon is smaller than the British Imperial gallon, 100 British being equivalent to 120 American gallons. Consequently, 100 British proof gallons are equal to 137 American proof gallons.

Similarly, in Holland a proof standard is recognised. Dutch proof contains 50 p.c. by volume of anhydrous alcohol at 15°. As in the United States, a series of alcoholometers are employed, differing only in regard to the range of their strength indications. The alcoholometer scale is divided into 28 principal divisions or degrees, which are equal in length, and again subdivided, each principal division representing $\frac{1}{100}$ of the volume of the instrument below the zero mark. Spirit tables based on the results of Baumhauer's investigations accompany the instruments and translate degrees on the scale into percentages of alcohol at 15° on which the revenue charge is based.

In Italy Tralles' alcoholometer is used officially. This instrument is made of glass, and at the standard temperature of 15·6° directly indicates the volume of alcohol contained in 100 volumes of spirit when measured at the same temperature. Indications at other temperatures are corrected by means of tables to true percentages by volume at 15·6°.

In Austria-Hungary an alcoholometer closely resembling Tralles', and indicating percentages of alcohol by volume at 15° is used. Its indications are uniformly higher than those of Tralles' to the extent of from one or two tenths per cent. Readings on this instrument are taken at the highest point of the capillary meniscus, which extends 1–2 mm. on the stem above the normal surface of the liquid.

Tralles' alcoholometer and tables are used commercially in Russia, but for Revenue purposes a metal hydrometer with nine poises similar in character to Sikes' hydrometer is official. On this instrument, however, Sikes' indications are reversed, so that '100' is made to represent strong spirit, and '0' distilled water. The hydrometer scale is arbitrary, and indications are interpreted into percentages by volume of Tralles' alcohol at the standard temperature of 15·6°.

Previous to the year 1887, Tralles' instrument was also used in Germany. It has now been replaced by a system of weight alcoholometry, based on Mendeléeff's data, whereby the proportion by weight of alcohol is determined. The official alcoholometers are made of glass, and

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·°6	Alcohol by weight (Germany)	Alcohol by volume at 15° (France)	Alcohol by volume at 15·6° (Tralles)	Russia	Holland	Spain (Cartier)	Switzerland (Beck)
	Overproof								
A.0.	73·5	198·2	98·2	98·9	99·1	—	25·3	43·5	42·6
A.1.	72·9	197·5	97·7	98·6	98·8	—	25	43·2	—
A.2.	72·2	196·8	97·2	98·2	98·4	—	—	—	41·8
A.3.	71·6	196·1	96·6	97·8	98·0	—	24·5	—	—
A.4.	71·0	195·3	96·1	97·5	97·7	—	—	42·2	40·9
A.5.	70·3	194·6	95·5	97·1	97·3	—	24	—	—
A.6.	69·6	193·8	94·9	96·7	96·9	—	—	—	—
A.7.	68·9	193·0	94·3	96·3	96·5	—	23·5	41·2	39·6
A.8.	68·2	192·2	93·7	95·9	96·1	—	—	—	—
A.9.	67·5	191·3	93·1	95·4	95·6	99·2	23	—	—
A.10 = 0	66·7	190·4	92·5	95·0	95·2	98·3	—	40·1	38·3
1	66·0	189·6	91·9	94·7	94·8	—	22·5	—	—
2	65·2	188·7	91·3	94·2	94·3	96·3	—	—	—
3	64·4	187·7	90·7	93·8	93·9	—	22	39·1	37·1
4	63·6	186·8	90·0	93·3	93·4	94·4	—	—	—
5	62·8	185·8	89·4	92·8	92·9	—	21·5	—	—
6	61·9	184·9	88·8	92·3	92·4	92·4	—	38·1	35·8
7	61·1	183·9	88·1	91·8	91·9	—	21	—	—
8	60·2	182·9	87·5	91·3	91·4	90·5	—	—	34·9
9	59·3	181·8	86·8	90·8	90·9	—	20·5	37·2	—
10	58·4	180·8	86·1	90·3	90·4	88·5	—	—	34·1
11	57·6	179·9	85·6	89·9	90·0	—	20	—	—
12	56·7	178·9	84·9	89·4	89·5	86·6	—	36·2	—
13	55·7	177·9	84·2	88·8	88·9	—	19·5	—	32·9
14	54·8	176·8	83·5	88·3	88·4	84·6	—	—	—
15	53·8	175·7	82·8	87·7	87·8	—	19	35·2	32
16	52·9	174·6	82·1	87·2	87·3	82·6	—	—	—
17	51·9	173·4	81·4	86·6	86·7	—	18·5	—	—
18	50·9	172·3	80·7	80·6	86·1	80·6	—	34·2	30·8
19	49·9	171·1	80·0	85·5	85·6	—	18	—	—
20	48·9	170·0	79·3	84·9	85·0	78·7	—	—	30
21	47·9	168·8	78·6	84·3	84·4	—	17·5	—	—
22	46·8	167·7	77·9	83·8	83·9	76·7	—	33	—
23	45·8	166·5	77·2	83·1	83·2	—	17·0	—	28·8
24	44·7	165·3	76·5	82·5	82·6	74·8	—	—	—
25	43·6	164·0	75·8	81·9	82·0	—	—	32	28
26	42·5	162·7	75·0	81·3	81·4	72·8	16·3	—	—
27	41·4	161·5	74·3	80·6	80·7	—	—	—	—
28	40·3	160·2	73·6	80·0	80·1	70·9	15·9	31·1	26·8
29	39·1	158·9	72·8	79·4	79·5	—	—	—	—
30	38·0	157·6	72·1	78·7	78·8	68·9	15·4	—	26
31	36·9	156·3	71·3	78·1	78·2	—	—	30·1	—
32	35·7	155·0	70·6	77·4	77·5	67	14·9	—	—
33	34·6	153·7	69·9	76·8	76·9	—	—	—	24·8
34	33·4	152·4	69·1	76·1	76·2	65	14·5	29·2	—
35	32·2	151·0	68·4	75·4	75·5	—	—	—	24
36	31·0	149·6	67·6	74·7	74·8	63·1	14	—	—
37	29·8	148·2	66·8	74·0	74·1	—	—	28·2	23·2
38	28·5	146·8	66·1	73·3	73·4	61·1	13·5	—	—
39	27·3	145·4	65·3	72·6	72·7	—	—	—	—
40	26·0	144·0	64·5	71·9	72·0	59·2	13·1	—	22
41	24·8	142·6	63·8	71·2	71·3	—	—	27	—
42	23·6	141·1	63·0	70·5	70·6	57·2	—	—	—
43	22·3	139·7	62·2	69·7	69·8	—	12·4	—	20·9
44	21·0	138·2	61·4	69·0	69·1	55·3	—	26·1	—
45	19·7	136·7	60·6	68·3	68·4	—	11·9	—	20·1
46	18·3	135·2	59·8	67·5	67·6	53·3	—	—	—
47	17·0	133·7	59·0	66·7	66·8	—	11·5	25·2	—
48	15·6	132·1	58·2	65·9	66·0	51·3	—	—	18·9
49	14·3	130·6	57·4	65·1	65·3	—	11	—	—
50	12·9	129·0	56·6	64·3	64·5	49·4	—	—	—
51	11·5	127·4	55·8	63·5	63·7	—	10·5	24	17·8
52	10·1	125·8	55·0	62·7	62·9	47·4	—	—	—

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·°6	Alcohol by weight (Germany)	Alcohol by volume at 150° (France)	Alcohol by volume at 15·6° (Tralles)	Russia	Holland	Spain (Cartier)	Switzerland (Beck)
	Overproof								
A.10=53	8·7	124·2	54·2	61·9	62·1	—	10·1	—	17
54	7·3	122·6	53·4	61·1	61·3	45·5	—	23·1	—
55	5·8	120·9	52·5	60·2	60·4	—	—	—	—
56	4·4	119·2	51·7	59·4	59·6	43·5	9·4	—	15·9
57	2·9	117·5	50·9	58·5	58·7	—	—	22·2	—
58	1·4	115·7	50·0	57·7	57·9	41·5	9	—	15·1
	Underproof								
59	0·2	114·0	49·2	56·8	57·0	—	—	—	—
60	1·7	112·2	48·3	55·9	56·1	39·5	—	21·3	—
61	3·3	110·5	47·5	55·0	55·2	—	8·3	—	14
62	4·8	108·7	46·6	54·1	54·3	37·6	—	—	—
63	6·4	106·9	45·8	53·2	53·4	—	7·9	—	13·3
64	8·1	105·0	44·9	52·3	52·5	35·6	—	20·1	—
65	9·7	103·1	44·0	51·3	51·5	—	—	—	—
66	11·4	101·2	43·1	50·4	50·6	33·6	7·2	—	12·2
67	13·1	99·3	42·1	49·4	49·6	—	—	—	—
68	14·9	97·2	41·1	48·4	48·6	31·6	6·8	19	—
69	16·7	95·1	40·2	47·3	47·5	—	—	—	11
70	18·6	93·0	39·2	46·3	46·5	29·7	—	—	—
71	20·5	90·8	38·2	45·2	45·4	—	6·1	18·1	—
72	22·4	88·6	37·2	44·1	44·3	27·7	—	—	9·9
73	24·4	86·4	36·2	43·0	43·2	—	5·7	—	—
74	26·4	84·2	35·2	41·9	42·1	25·7	—	—	—
75	28·5	81·8	34·1	40·7	40·9	—	—	16·9	8·8
76	30·7	79·4	33·0	39·5	39·7	23·7	5·1	—	—
77	32·9	76·9	31·9	38·3	38·5	—	—	—	8·1
78	35·3	74·3	30·7	36·9	37·1	21·8	—	16·1	—
79	37·7	71·4	29·5	35·5	35·7	—	4·4	—	—
80	40·3	68·5	28·2	34·0	34·2	19·8	—	—	7
81	42·9	65·4	26·9	32·5	32·7	—	4·0	—	—
82	45·7	62·3	25·6	31·0	31·2	17·9	—	15	—
83	48·6	58·9	24·2	29·3	29·5	—	3·6	—	6
84	51·7	55·4	22·7	27·5	27·7	15·9	—	—	—
85	54·8	51·7	21·1	25·6	25·8	—	—	14·1	—
86	58·2	47·9	19·5	23·7	23·9	13·9	3·0	—	4·9
87	61·5	44·1	18·0	21·8	22·0	—	—	—	—
88	65·0	40·2	16·4	19·9	20·1	11·9	—	13·3	—
89	68·4	36·2	14·7	18·0	18·1	—	2·3	—	3·8
90	71·9	32·2	13·1	16·0	16·1	9·9	—	—	—
91	75·2	28·4	11·5	14·1	14·2	—	1·9	12·4	3·1
92	78·4	24·7	10·0	12·3	12·4	7·9	—	—	—
93	81·4	21·3	8·6	10·6	10·7	—	1·5	—	—
94	84·4	17·9	7·2	8·9	9·0	6	—	11·6	2·1
95	87·3	14·6	5·8	7·2	7·3	—	—	—	—
96	90·0	11·4	4·6	5·6	5·7	4	0·9	—	—
97	92·6	8·4	3·4	4·1	4·2	—	—	10·8	1
98	95·1	5·6	2·2	2·7	2·8	2	—	—	—
99	97·6	2·8	1·1	1·4	1·4	—	—	—	—
100	100·0	0·0	0·0	0·0	0·0	0	0	10·1	0·1

graduated to show percentages of alcohol by weight at 15°—apparent percentages at other temperatures being converted into true percentages by means of tables. Duty is, however, charged on the volume of anhydrous alcohol present in a spirit when measured at 15·6°. This system is therefore analogous to the British, with the exception that the dominant temperature at which British proof-strengths are computed is 10°.

In France Gay-Lussac's original volume alcoholometer and tables have been corrected to the new values for densities of mixtures of alcohol and water determined by the 'Bureau national des poids et mesures' (1884). The density of anhydrous alcohol at 15°/15° is given as 0·79433 in vacuum, as against 0·7947 assumed by Gay-Lussac, and the difference between the graduations of the old and new official instruments reaches a maximum of 0·4 p.c. for spirits containing from 20 to 21 p.c. of alcohol by volume. Thus 20° at a temperature of 15° on the new legal centesimal alcoholometer indicates spirit containing 20 p.c. by volume of alcohol, and corresponds to 20·4° on Gay-Lussac's original instrument. The French spirit tables indicate, at temperatures extending from

0° to 30°, the percentage by volume of alcohol which a liquid contains at 15°.

Previous to the adoption of Gay-Lussac's alcoholometer and tables by the French Government, Cartier's areometer was used as the Revenue instrument. Its stem is graduated from 10 to 45 in divisions of equal length, and indicates the concentration of a spirituous liquid by arbitrary degrees, which serve as spirit-strengths for charging duty. Cartier's areometer is still used in Spain and South America.

In Switzerland, Beck's hydrometer is used for spirit assaying, and, like Cartier's instrument, of which it is a modification, floats at the lowest indication in distilled water at 12·5° (10°R.).

By means of the table on p. 67 the indications of any one of these instruments at 15·6° can be converted into degrees of any other, and British fiscal strengths compared with those of other countries.

An indispensable step to a correct assay of spirit is the removal of any foreign matter which may be in solution in the alcoholic mixture. In the case of potable spirits, wines, liqueurs, &c., the spirit is freed from saccharine and other dissolved matter by distillation. The distillation of a strong spirituous liquid into its own volume so as to obtain an accurate determination of the amount of alcohol present is impracticable with the apparatus and the methods of distillation commonly used, so that although it is possible to distil without loss spirits of underproof strength into the same volume, it is necessary to dilute overproof spirits and distil into two, three, or four times the original volume. The amount by which the true alcoholic strength of brandy or rum differs from the apparent strength, as indicated by the hydrometer or a density determination, is termed the 'obscuration.'

In the case of medicinal preparations, flavouring essences, &c., which yield distillates containing essential oils and volatile substances, special treatment is necessary before a pyknometrical determination of spirit is possible. In these circumstances the sample or distillate is mixed with water in a separator so that the mixture shall contain not more than 20–25 p.c. by volume of alcohol, and common salt is added in quantity sufficient to saturate the liquid. The mixture is then shaken vigorously with 50–100 c.c. of light petroleum, and after remaining a short time, the aqueous layer is extracted, if necessary, a second time with petroleum (for instance when chloroform or ether is present), and finally drawn off into a flask and distilled. In the case of soap liniments and similar preparations, dilute sulphuric acid is used instead of salt, and the aliphatic acids and volatile matters removed by petroleum before distilling (Chem. Soc. Trans. 1903, 314). Preparations containing iodine are decolourised with sodium thiosulphate, and excess of caustic soda added to prevent decomposition of the tetrathionate during distillation. Similarly, volatile acids must be neutralised, and ammoniacal liquids distilled from dilute sulphuric acid solution.

For the estimation of ethyl alcohol in fusel oil, or liquids containing fusel oil, the salt-petroleum process may be employed, but as the higher alcohols cannot be wholly eliminated by this method, the specific refraction of the distillate is determined by the Zeiss Immersion Refractometer. The refractions of mixtures of ethyl alcohol and water have been determined at various temperatures by Wagner and Schultze (Zeitsch. anal. Chem. 1907, 508) and others, and a near approximation to the true alcoholic content of a fusel oil mixture, treated as above described, can be obtained by applying to the apparent percentage by volume of alcohol, as indicated by the density of the distillate, a subtractive correction of 0·5 p.c. for each degree of difference between the refractometer reading as found at 15·6°, and that required for a mixture of ethyl alcohol and water corresponding to the ascertained density. This method of eliminating foreign matters in spirit assaying, from a knowledge of their influence on the specific refractions of aqueous alcoholic mixtures, is capable of wide application, and has been utilised, for instance, by Leach and Lythgoe (Amer. Chem. J. 1905, 964) for determining the proportion of methylated spirits in a spirituous liquid (*v.* REFRACTOMETER). J. H.

ALCORNIN or **ALCORNOL.** An alcohol, $C_{22}H_{34}O$, of the nature of phytosterol found in Alcornoco bark (Hartwich and Dünnenberger, Arch. Pharm. 1900, 341).

ALCOVINOMETER. An instrument for determining the alcoholic content of a wine by observing its ascent in a capillary tube.

ALDEHYDE *Acetaldehyde* C_2H_4O or $CH_3{\cdot}COH$. A product of the oxidation of ordinary (ethylic) alcohol. Aldehyde occurs, together with its polymerides metaldehyde and paraldehyde, in the 'first runnings' from the stills in the rectification of alcohol which has been filtered through charcoal (Krämer and Pinner, Ber. 2, 403; 4, 787; Johnson, J. Soc. Chem. Ind. 8, 57; Hewitt, *ibid.* 21, 97); the best yield is obtained from the alcohol manufactured from potatoes and from the sugar beet. It is also present in crude wood spirit (Krämer and Grodzki, Ber. 9, 1921); in crude petroleum (Robinson, J. Soc. Chem. Ind. 18, 232); in wine during the process of ageing (Trillat, Compt. rend. 136, 171); and in certain circumstances in the fermentation products of alcohol (Trillat, Compt. rend. 146, 645; Trillat and Souton, 146, 996; Kayser and Demolon, 146, 783).

Aldehyde is also formed when calcium formate is heated with calcium acetate (Limpricht, Annalen, 97, 369), and when lactic acid and the lactates are distilled with manganese dioxide and sulphuric acid (Städeler, Annalen. 69, 333); it is also one of the products of the dry distillation of sugar (Völckel, Annalen, 87, 303).

Preparation.—Aldehyde is formed by the oxidation of alcohol by means of platinum black (Döbereiner, Gm. 8, 274), of manganese dioxide and sulphuric acid (Liebig, Annalen, 14, 133), of potassium dichromate and sulphuric acid (Städeler, J. 1859, 329), of metallic catalysers (Bouveault, Bull. Soc. chim. 1908, 3, 117; Sabatier and Senderens, Compt. rend. 136, 738), or when alcohol is passed through an iron tube heated to 710°–750° (Ipateiff, Ber. 34, 596).

According to Lang (J. Soc. Chem. Ind. 22, 571), the most useful oxidising agents for converting alcohol to aldehyde are the manganic salts. When prepared by Liebig's method, 2 parts of 80 p.c. alcohol are heated with 3 parts of manganese dioxide, 3 parts of

sulphuric acid, and 2 parts of water, and the distillation carried on until the distillate begins to show an acid reaction; this point is reached when about three parts have collected in the well-cooled receiver. The distillate containing alcohol, acetal and ethereal salts is then distilled with an equal weight of calcium chloride, and 1½ parts collected; this is again rectified with an equal weight of calcium chloride and ¾ part distilled over. The product so obtained is nearly anhydrous, but still contains alcohol and small quantities of ethereal salts; to free it from these, it is dissolved in 2 vols. of ether, saturated with ammonia in the cold, and the aldehyde-ammonia which separates is collected, dissolved in water, distilled with dilute sulphuric acid in a water-bath, and the distillate rendered anhydrous by rectification over calcium chloride at as low a temperature as possible.

Improved methods and apparatus for oxidising alcohol into aldehyde are described by Boult (J. Soc. Chem. Ind. 15, 668; Fournier, *ibid.* 16, 695).

Commercially, aldehyde is obtained from the 'first runnings' of the alcohol stills. A special form of still in which the separation of aldehyde from alcohol is brought about during the rectification of the latter is figured and described by Galland (Dingl. poly. J. 259, 225).

Substituted acetaldehydes applicable to perfumery can be obtained by condensing a ketone with a halogen or amino substituted acetic ester in the presence of sodium. The α-hydroxyacrylic ester thus obtained is saponified and decomposed by heat or distillation under reduced pressure (J. Soc. Chem. Ind. 23, 455).

Properties.—Aldehyde is a colourless liquid b.p. 20·8°, m.p. −120·7°, and sp.gr. 0·80092 at 0° (Kopp, Annalen, 64, 214); 0·79509 at 10°, 0·79138 at 13°, 0·78761 at 16° (Perkin, Chem. Soc. Trans. 45, 475). It has an extremely pungent suffocating odour; it is very inflammable, and burns with a feebly luminous flame.

It is soluble in all proportions in alcohol, ether, and water, and is separated from the aqueous solution as an ethereal layer on addition of calcium chloride. When heated with aqueous soda, potash, or barium hydroxide, so-called aldehyde resin is obtained as a brown mass (Liebig, *l.c.*; Weidenbusch, Annalen, 66, 153; Lederer, Monatsh. 22, 536). Sodium amalgam converts aldehyde into ethyl alcohol, a small quantity of β-butyleneglycol, which is also formed by the action of magnesium amalgam (Meunier, Compt. rend. 134, 472; Tistschenko and Grigoreeff, J. Russ. Phys. Chem. Soc. 38, 540; Voronkoff, *ibid.* 38, 547), being formed simultaneously (Kekulé, Annalen. 162, 310). With sodium, acetaldehyde reacts violently, producing the compound $CH_2:CH\cdot ONa$, which rapidly polymerises to a brown substance, whilst if the reaction takes place in presence of benzoic chloride in ethereal solution aldehydoaldolbenzoate $C_{13}H_{16}O_4$, m.p. 86°–87°, is formed (Freer, Amer. Chem. J. 18, 552; Annalen, 293, 326). Phosphorus pentachloride reacts with it, yielding ethylidene dichloride (Geuther, Annalen, 105, 323).

In presence of reduced nickel hydrogen reduces aldehyde to ethyl alcohol, a good yield and pure product being obtained (Sabatier and Senderens, Compt. rend. 137, 301). With potassium permanganate, acetic acid is formed, but in presence of excess of potash, oxalic and carbonic acids are also formed (Denis, Amer. Chem. J. 38, 561).

When subjected to electrolysis in faintly alkaline or neutral solution it is decomposed into alcohol and acetic acids (Slaboszewicz, Chem. Zentr. 1903, i. 279; Law, Chem. Soc. Trans. 1905, 198; Jackson and Laurie, *ibid.* 1906, 156), whilst when heated alone to high temperatures carbon monoxide and methane are the chief products (Bone and Smith, Chem. Soc. Trans. 1905, 910).

Acetaldehyde and its dimethyl derivative have antiseptic properties (Coblenz, J. Soc. Chem. Ind. 17, 728; Pasqualis, Chem. Zentr. 1897, ii. 10, 12). It is also useful in photographic developing (Seyewetz, Bull. Soc. chim. 19, (3) 134), and the vapour or solution in alcohol or benzene slowly hardens dry gelatine films (Beckmann, Chem. Zentr. 1896, ii. 930).

Aldehyde readily polymerises in the presence of small quantities of various substances, such as sulphuric acid, phosgene, zinc chloride, hydrogen chloride, sulphur dioxide, the halogens, particularly iodine, &c., and two compounds are obtained the relative quantities of which depend upon the temperature; the chief product being *metaldehyde* $(C_2H_4O)_3$ (Hanriot and Oeconomides, Ann. Chem. Phys. [5] 25, 227; McIntosh, Chem. Soc. Trans. 1905, 790; Zecchini, Gazz. chim. ital. 22, ii. 586), when the action takes place in a freezing mixture; and the isomeric *paraldehyde* (elaldehyde) when it occurs at the ordinary temperature (Kekulé and Zincke, Annalen, 162, 125; Desgrez, Bull. Soc. chim. 11, (3) 362; Wachhausen, Chem. Zentr. 1897, i. 493; Ciamician and Silber, Ber. 35, 1080).

Paraldehyde is a colourless liquid, crystallising below 10° in large transparent prisms; b.p. 124° at 759·8 mm. and sp.gr. 0·998 at 15° (Kekulé and Zincke); sp.gr. 0·99925 at 15° (Perkin, Chem. Soc. Trans. 45, 479); b.p. 123·2°–123·5° at 744 mm. (Brühl, Annalen, 203, 26). When condensed with hydroxyquinol, it produces yellow dyes (Liebermann and Lendenbaum, Ber. 37, 1171, 2728).

Metaldehyde crystallises in needles or tetragonal prisms, sublimes without previous fusion at 112°–115°, and when heated in sealed tubes at 120° is entirely reconverted into ordinary aldehyde (Friedel, Bull. Soc. chim. 9, (3) 384). According to Troeger (Ber. 25, 3316), after standing for ten years a sample was converted into aldehyde and paraldehyde, but according to Hantzsch and Oechslin (Ber. 40, 4341), metacetaldehyde is not isomeric with paracetaldehyde, and is quite stable when pure. Orndorff and White (Amer. Chem. J. 16, 43) state that when it is allowed to stand for some time the metaldehyde is converted into tetraldehyde $(C_2H_4O)_4$.

Neither polymeride is resinised by aqueous soda or potash, but in other reactions they behave generally as ordinary aldehyde and yield similar products (Kekulé and Zincke).

Reactions.—Aldehyde in aqueous solution very readily reduces an ammoniacal solution of silver nitrate giving a bright metallic mirror. Acetaldehyde (and all aldehydes which are stable in aqueous soda solution) can be detected by adding to a solution of the suspected

substance in dilute alkali a fresh solution of 1 part of paradiazobenzenesulphonic acid in 60 parts of water rendered alkaline with a little soda, and then some sodium amalgam; if an aldehyde is present, a reddish-brown colour is developed after the mixture has stood for 10–20 minutes (Penzoldt and Fischer, Ber. 16, 657).

A solution of rosaniline decolourised by sulphurous acid (Villiers and Foyolle, Compt. rend. 119, 75), or magenta bleached by sunlight (Blaser, Chem. Zentr. 1899, ii. 848), regains its original colour on addition of an aldehyde. This reaction is due to the formation of coloured compounds by the condensation of the aldehyde and magenta (Urbain, Bull. Soc. chim. 1896, iii. 15, 455). With salts of *m*-diamines aldehydes give coloured solutions with intense greenish fluorescence (Bitto, Frdl. 36, 369). With sodium nitroprusside and alkali acetaldehyde gives a cherry-red colouration, whilst if trimethylamine is first added a blue colour is produced (Bitto, Annalen, 267, 372; 269, 377; Denigès, Bull. Soc. chim. 17, (3) 381; Simon, Compt. rend. 125, 1105; Bull. Soc. chim. 19, (3) 297). Thiosemicarbazide mixed with an aldehyde in acetic, alcoholic, or aqueous solution yields characteristic thiosemicarbazones. Acetaldehydethiosemicarbazone has m.p.146°(Freund and Schander, Ber. 35, 2602).

Other tests for aldehydes are described by (Ihl, Chem. Zeit. 14, 1571; Doebner, Ber. 27, 352, 2020; Lumière and Seyewetz, Bull. Soc. chim. 19, (3) 134; Rimini, Atti Real. Acad. Lincei, 1901, 10, 355; Murco, Compt. rend. 31, 943; Riegler Frdl. 42, 168; Behrens, Chem. Zeit. 26, 1125; Sadtler, J. Soc. Chem. Ind. 23, 387; Prud'homme, Bl. Soc. Ind. Mulhouse, 1904, 74, 169; Leys, J. Pharm. Chim. 1905, 22, 107; Auld and Hantzsch, Ber. 38, 2677.

Aldehyde readily yields condensation compounds; thus when allowed to remain in the cold with dilute hydrochloric acid, or with aqueous solutions of zinc chloride or of salts having an alkaline reaction, such as potassium carbonate, aldol is obtained, whilst crotonaldehyde is formed when it is heated with concentrated hydrochloric acid (Kekulé, Annalen, 162, 92; Kling and Roy, Compt. rend. 144, 1111).

Aldehyde has also been condensed with other aldehydes and ketones (Wallach, Chem. Zentr. 899, ii. 1024; Schmalzhoffer, Monatsh. 211, 671; Wogrinz, *ibid.* 22, 1; Weiss, *ibid.* 25, 1065; Schachner, *ibid.* 26, 65; Salkind, J. Russ. Phys. Chem. Soc. 37, 484; Rainer, Monatsh. 25, 1035; Ehrenfreund, *ibid.* 26, 1003); with amines (Eibner and Peltzer, Ber. 33, 3460; Eibner, Annalen, 328, 121; Knoevenagel, Ber. 37, 4461); with rhodanic and substituted rhodanic acids forming stable dyeing compounds (Andreasch and Zipser, Monatsh. 24, 499; 26, 1191; Zipser, *ibid.* 23, 592; Stachetz, *ibid.* 26, 1209; Bergellini, Atti Real. Acad. Lincei, 15, 35, 181; Andreasch, Monatsh. 27, 1211; 29, 399; Wagner, *ibid.* 27, 1233); with methyl ketole forming leuco- bases of the dyes of rosaniline type (Freund and Lebach, Ber. 36, 308; Freund, Ber. 37, 322); with indole dyes, also forming leuco- bases (Loew, Ber. 36, 4326); with cyanides and cyanacetic esters (Claisen, Ber. 25, 3164; Barbier and Bouveault, Compt. rend. 120, 1269; Kohn, Monatsh. 19, 519; Wade, Chem. Soc. Proc. 1900, 156; Bertini, Gazz. chim. ital. 31, i. 265; Fiquet, Bull. Soc. chim. 7, (3) 767); with phenyl hydrazones (Fischer, Ber. 29, 793; 30, 1240; Pechman, Ber. 31, 2123; Bamberger and Pemsel, Ber. 36, 85; Lockmann and Liesche. Annalen, 342, 14; Medvedeff, Ber. 38, 1646, 2283; Maurenbrecher, Ber. 39, 3583). Substances capable of use in perfumery can be obtained by condensing aldehydes with negatively mono- substituted acetic acids in presence of ammonia or a primary or secondary amine (J. Soc. Chem. Ind. 24, 689, 1323). (For compounds of other substances with aldehydes, *see* Hooker and Carnell, Chem. Soc. Proc. 1893, Fischer, Ber. 27, 165; Claisen, Annalen, 237, 261; Conneler, Chem. Zeit. 20, 585; Kietreiber, Monatsh. 19, 735; Bamberger and Müller, Ber. 27, 147; Rassow, J. pr. Chem. 172, 136, 129; Betti, Gazz. chim. ital. 30, ii. 310; 33, i. 27; Koenigs, Ber. 34, 4336; Moureu and Desmots, Compt. rend. 134, 355; Knoevenagel, Ber. 36, 2136; Hann and Lapworth, Chem. Soc. Trans. 1904, 46; Simon and Conduché, Compt. rend. 138, 977; Darzens, Compt. rend. 142, 214; Eissler and Pollock, Monatsh. 27, 1129; Rolla, Gazz. chim. ital. 37, 623; Senier and Austin, Chem. Soc. Trans. 1907, 1233; Wohl, Ber. 40, 4679; Braun, Ber. 41, 2169; Zeisel and Bitto, Monatsh. 29, 591.)

Additive compounds.—Aldehyde not only shows a strong tendency to yield polymerides and condensation compounds, but unites directly with a large number of substances.

(1) Compounds with alcohols (*v.* ACETAL).

(2) Compounds with acids:—Geuther, Annalen, 106, 249; Lieben, *ibid.* 106, 336; 178, 43; Rübencamp, *ibid.* 225, 279; Schiff, Ber. 9, 304; Ponzio, J. pr. Chem. 161, 431; Schroeter, Ber. 31, 2189; Annalen, 303, 114; Delépine, Compt. rend. 133, 876; McIntosh, Amer. Chem. J. 28, 588.

(3) Compounds with alkaline sulphites:—Aldehyde forms definite crystalline compounds when dissolved in concentrated aqueous solutions of the acid sulphites (bisulphites) of the alkali metals. The *potassium* salt $C_2H_4O,KHSO_3$ crystallises in indistinct needles; the *sodium* salt $C_2H_4O,NaHSO_3+\frac{1}{2}H_2O$, in fine needles or nacreous plates. The ammonium compound has the formula $C_2H_4(OH)SO_3{\cdot}NH_2$. These salts are almost insoluble in excess of the sulphite, and separate in the crystalline state; from them aldehyde can be obtained by distillation with a stronger acid, an alkaline carbonate, or by alkali nitrites (Bunte, Annalen, 170, 305; Freundler and Bunel, Compt. rend. 132, 1338; Seyewetz and Burdin, Compt. rend. 141, 259; Rosenheim, Ber. 38, 2005; Coppock, Chem. News, 1907, 225). With hyposulphites in neutral or acid solutions aldehyde hyposulphites are obtained; $2RCHO,M_2S_2O_4$ (J. Soc. Chem. Ind. 25, 475); by varying the condition sulphoxylates of type $RCH_2{\cdot}SO_3M$ can be formed (D. R. P. 180529). Crystalline thioaldehydes are obtained by the action of hydrogen sulphide on an acidified alcoholic solution of aldehyde (Baumann and Fromm, Ber. 22, 2600; Ber. 24, 1419, 1457; Klinger, Ber. 32, 2194; Drugman and Stockings, Chem. Soc. Proc. 1904, 116; Vanino, J. pr. Chem. 185, 367).

(4) Compound with ammonia:—*Aldehyde-ammonia* $C_2H_4O{\cdot}NH_3$, obtained by leading dry ammonia into aldehyde in ethereal solution

(Liebig, Annalen, 14, 144; Jean, Bull. Soc. chim. 13, (3) 474; Trillat, *ibid.* 13, (3) 689; Delépine, Compt. rend. 125, 951; 128, 105; 137, 984; 144, 853; Coninck, Compt. rend. 126, 1042; Tschitschibabin, J. Russ. Phys. Chem. Soc. 37, 1229; Duden, Bock and Reid, Ber. 38, 2036; Ciamician and Silber, Ber. 38, 1671; 39, 3942), crystallises in large rhombohedra, melts at 70°–80°, boils at 100° without decomposition, and is decomposed into its constituents on distillation with dilute acids. When hydrogen sulphide is passed through a mixture of aldehyde ammonia and ether a crystalline substance SH·CHMe·NH·CHMeOH, m.p. 60°–63°, is obtained (Chabrié, C. R. Soc. Biol. 1896, 3, 72).

(5) Compounds with hydrocyanic acid:—(Tiemann, Ber. 14, 1965; Strecker, Annalen, 91, 349; Erlenmeyer and Passavant, *ibid.* 200, 120).

(6) Compounds with metallic salts:—With mercuric sulphate it forms the compound SO_4:$(HgO)_2$: HgC_2H_4O (Denigès, Compt. rend. 128, 429); with mercuric nitrate, $C_2Hg_2NO_4H$ (Hofmann, Ber. 31, 2212); and with mercuric acetate alkaline solution at 0°, CMe·HO·HgO (Lasserre, J. Pharm. 1905, 22, 246). With gold chloride it forms a coloured colloidal solution (Garbowski, Ber. 36, 1215); and with magnesium bromide, the compound $MgBr_2,3CH_3CHO$ (Menschutkin, Zeitsch. anorg. Chem. 53, 26).

Substitution-derivatives. — The action of chlorine on aldehyde has been studied by Wurtz (Annalen, 102, 93), Wurtz and Voigt (Bull. Soc. chim. 17, 402), and by Pinner (Annalen, 179, 21; Coblenz, *l.c.*; Freundler, Bull. Soc. chim. 1, (4) 66; Freundler, Compt. rend. 143, 682). Pinner finds that when chlorine is passed into ordinary aldehyde at 10°, metaldehyde and paraldehyde are first formed, and these subsequently yield substitution-derivatives, of which chloral is the chief product, butyric chloral and dichloraldehyde being formed in smaller quantity. The following derivatives have been prepared:—*Chloraldehyde* $CH_2Cl·CHO+\frac{1}{2}H_2O$ (Natterer, Monatsh. 3, 446); *dichloraldehyde*, $CHCl_2·CHO$ (Grimaux and Adams, Bull. Soc. chim. 34, 29; Wohl and Roth, Ber. 40, 212); *trichloraldehyde* (*v.* CHLORAL).

The bromine derivatives, and the action of bromine on aldehyde, have been examined by Pinner (Ber. 7, 1499, and *l.c.*; Bugarsky, Zeitsch. physikal. Chem. 48, 63; Freundler, Compt. rend. 140, 1693; Mauguin, Compt. rend. 147, 747).

Aldehyde blue is obtained by treating pararosaniline with aldehyde or, better, paraldehyde in aqueous acid solution, and precipitating the dye with sodium chloride. It is soluble in alcohol and ether, and when treated with strong hydrochloric acid is converted into a reddish yellow base which shows all the properties of a rosaniline dye (Gattermann and Wichmann, Ber. 22, 227). By slightly varying the conditions in the preparation of aldehyde blue, *aldehyde green* can also be obtained (Miller and Plüchl, Ber. 24, 1700).

ALDEHYDES. The name aldehyde originally assigned to the compound obtained by the limited oxidation of ethyl alcohol, has come to possess a wider signification, and is now used as a generic term for a class of organic substances which are similarly derived from the primary alcohols. In composition the aldehydes differ from the alcohols from which they are derived by containing two atoms of hydrogen fewer in the molecule; whilst in their chemical behaviour they all exhibit the general properties of the typical member of the series, acetaldehyde.

There are general methods for preparing aldehydes: (1) By the action of organomagnesium compounds on the esters of orthoformic ester thus:

$$HC(OR)_3 + R'MgI = ROMgI + R'HC(OR)_2$$
$$R'HC(OR)_2 + H_2O = R'HCO + 2R·OH$$

(Tschitschibabin, Ber. 37, 186; Gattermann and Maffezzoli, Ber. 36, 4152; Williams, Chem. Soc. Proc. 1906, 22). (2) By decomposing with water the products of reaction between di-substituted amino-formaldehydes on alkyl, aryl, or hydroxyl magnesium halides (J. Soc. Chem. Ind. 23, 1237; Bouveault, Bull. Soc. chim. 31, (3) 1306, 1322). (3) By the action of organo-magnesium compounds on formic acid or alkyl formates (J. Soc. Chem. Ind. 24, 690; Chem. Zentr. 29, 667; D. R. P. 157573).

Other methods are described by Stoermer (Ber. 39, 2288); Blaise (Compt. rend. 138, 697); Faworsky (J. Russ. Phys. Chem. Soc. 38, 741); Tiffeneau (Compt. rend. 37, 1260); Behal and Sommelet (D. R. P. 177614, Compt. rend. 138, 89); Guerbet (Compt. rend. 146, 132); Mossler (Monatsh. 29, 69); Merling (Ber. 41, 2064, 2217) Aliphatic dialdehydes have been prepared by Wohl and Schweitzer (Ber. 39, 890); Suais (Bl. Ind. Mulhouse, 1907, 75).

ALDEHYDE GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ALDEHYDINE *v.* BONE OIL.

ALDEHYDINES. Compounds formed by the condensation of ortho-diamines with aldehydes (Ladenburg, Ber. 10, 1126) (*v.* AMINES).

ALDER BARK. (*Aune*, Fr.; *Erle*, Ger.) *Alnus glutinosa* (Gaert.). Used for tanning and dyeing. The percentage of tannin varies from 16 to 18 (Eitner, Zeit. f. d. Chem. Grossgew. 3, 668; 4, 279).

The tannin appears to be a methyl tannin like that of the oak; it gives a reddish-blue precipitate with ferrous acetate, an olive-green precipitate with ferrous sulphate, and is precipitated by a gum solution.

A solution of the bark is employed for obtaining black, greys, and browns on linen; in Germany for reds; and in Kamchatka for colouring skins a red tint.

ALE *v.* BREWING.

ALEMBROTH, SALT OF. A compound of mercuric chloride and sal ammoniac

$$2NH_4Cl,HgCl_2,H_2O.$$

formed by mixing the two salts in suitable proportions. Also called by the alchemists Salt of Wisdom.

ALEURITES CORDATA (Steud.). The seeds of this euphorbiaceous plant, which is found largely in Japan, yield Japanese wood-oil (*q.v.*).

ALEURONE GRAINS. Organised granules deposited in the cells of many seeds of plants, generally near the exterior, in which the proteins are mainly concentrated. They were so named by Hartig, who first described them. In many plants, the aleurone grains possess the shape of

crystals. Botanists, indeed, regard them as consisting of two parts: (1) a *crystalloid*, crystal-like protein body, and (2) one or more rounded *globoids* mainly composed of mineral matter, in which phosphoric acid, lime, and magnesia are usually the largest constituents.

When the aleurone grains exhibit the form of crystals, it is generally found that they are soft and swell up if treated with weak acids or alkalis. The term 'crystalloid,' as used by botanists in this connection, has reference to the appearance of the aleurone grains, and not to their property of diffusion when dissolved through membranes. According to Tschirch and Kritzler (Chem. Zentr. 1900, ii. 585), the aleurone grains of a variety of plants consist mainly of globulins. The crystalloids consist of at least two globulins, which are soluble in dilute, but insoluble in concentrated saline solutions (*e.g.* ammonium sulphate, sodium chloride with trace of acetic acid, potassium dihydrogen phosphate). A small amount of an albumose is also probably present. The globoids contain a globulin and mineral matter, especially calcium, magnesium, and phosphoric acid; they are soluble in concentrated solutions of ammonium sulphate, acidified sodium chloride, or potassium dihydrogen phosphate. The grains with their enclosures are reserve-food materials which are consumed when the seed germinates. They originate as liquid 'vacuoles,' in which an increasing amount of protein material is gradually deposited. The germinating power of seeds probably depends upon the solubility of the crystalloids in dilute sodium chloride solution.

According to Posternak (Compt. rend. 1905, 140, 322), aleurone grains often contain anhydro-oxymethylene diphosphoric acid (phytine). He found the following amounts of nitrogen and mineral substances in the aleurone grains of (1) spruce fir, (2) sunflower, (3) hemp, (4) white lupin:—

	N	K	Ca	Mg	Fe	Mn	P	S	Si
1.	12·97	2·50	0·37	1·25	0·09	0·25	2·67	0·64	0·35
2.	10·22	2·20	0·33	1·46	0·05	trace	2·78	0·64	0·24
3.	12·88	2·71	0·27	1·67	0·05	trace	3·83	0·81	0·36
4.	10·70	—	0·11	0·28	—	0·11	0·61	—	0·01

Sodium and chlorine were not found. H. I.

ALFA *v.* HALFA.

ALFALFA. The Spanish name for lucerne, *Medicago sativa* (Linn.).

ALGÆ. (*Varech* or *Algues*, Fr.; *Algen*, Ger.) A class of cryptogamous plants including the green, brown, and red seaweeds and vegetable plankton growing in sea-water, and allied mainly green fresh-water plants, including diatoms, desmids, and 'conferva'-like forms. Many of the salt-water species are edible; none of them is poisonous.

Rhodymenia palmata (Linn.) (dulse, dylish, or dellish) and *Alaria esculenta* (murlins) are used as food by the peasantry of the Highlands and of Ireland. *Porphyra laciniata* (Lightf.) (laciniated purple laver), very abundant on the British coasts, is sold in England as laver, in Ireland as sloke, and in Scotland as slaak. *Chondrus crispus* (Linn.) (carrageen, Irish or pearl moss) is collected on the west coast of Ireland, and is frequently used there by painters and plasterers as a substitute for size. It is also used in making jellies, &c., in medicine; and a thick mucilage scented with some prepared spirit is sold as 'bandolin,' 'fixature,' or 'clysphitique,' and is employed for stiffening silks.

Amongst other algæ having an economic value are Ceylon moss or edible moss (*Gracilaria lichenoides*), found in the Indian archipelago; the agar-agar of Malacca, or agal-agal of China, which is derived from *Gracilaria lichenoides*, *Eucheuma spinosum* (Linn.) and other algae (*see* AGAR). The substance is now much used in bacteriological research as a nutrient jelly; for gumming silks, paper, &c., and for making a paste not liable to be eaten by insects.

Manna, or mannite, can be obtained from *Laminaria saccharina* (Lamx.) or sugar wrack, found on sandy shores, attached to pebbles.

The following table shows the composition of various species of algæ; the quantity of nitrogen in some of them is remarkably large:—

Alga	Water	Dry matter	Per cent. nitrogen in dry matter	Protein contained in dry matter
Chondrus crispus, bleached from Bewlay Evans	17·92	82·08	1·534	9·587
Chondrus crispus bleached second experiment	19·79	80·21	1·485	9·281
Chondrus crispus, unbleached Ballycastle	21·47	78·53	2·142	12·387
Chondrus crispus, unbleached, second experiment	19·96	80·04	2·510	15·687
Gigartina mamillosa, Ballycastle	21·55	78·45	2·198	13·737
Laminaria digitata, or dulse tangle	21·38	78·62	1·588	9·925
Rhodymenia palmata	16·56	83·44	3·465	21·656
Porphyra laciniata	17·41	82·59	4·650	29·062
(*Sarcophyllis*) *edulis*	19·61	80·39	3·088	19·300
Alaria esculenta	17·91	80·09	2·424	15·150

In addition to the large amount of chlorine in marine algæ (up to 38 p.c. of the ash) there are often not inconsiderable quantities of iodine, the presence of which is responsible for the employment of seaweeds in the composition of certain 'anti-fat' specifics.

Certain algæ are characteristic of water containing sewage and putrefactive substances in quantity, and some algæ play an important *rôle* in the disinfection of polluted rivers.

ALGAROBILLA. Algarobilla consists of the pods of *Cæsalpina brevifolia*. The tannin, which appears to be a mixture of allagetannin and gallotannin, lies in semi-resinous particles

adhering loosely to the somewhat open framework of the fibre. It is one of the strongest tannin matters known, and contains on the average 45 p.c. In character it resembles divi-divi, and its extract is somewhat prone to fermentation. It is very suitable for tanning and also for dyeing purposes.

ALGAROTH, POWDER OF. *Pulvis Algarothi, English Powder.* A crystalline oxychloride of antimony, obtained by pouring antimony chloride into hot water. Used in the preparation of tartar emetic (*v.* ANTIMONY).

ALGIN. A nitrogenous body obtained from seaweed, somewhat resembling albumen (*v.* IODINE).

ALGODONITE. A copper arsenide of a steel-grey colour. Found in the Lake Superior copper-mining district.

ALHAGI CAMELORUM (Fischer), **JAWÁSA, or JAWANI.** A leguminous thorny shrub, widely spread from Greece to dry parts of India, where a drug extracted from it is used for rheumatism, and also as a laxative and diuretic (Pharm. J. [3] 9, 145).

ALIZARIN AND ALLIED COLOURING MATTERS. Madder, *Rubia tinctoria*, which was for a long time used on a large scale in the 'Turkey-red' industry, contains two colouring matters, alizarin and purpurin, of which the former is by far the more important.

Alizarin is not found ready-formed in the madder-root, but exists there as a glucoside called 'ruberythric acid,' which when allowed to ferment, or when boiled with dilute acid, splits up readily into alizarin and glucose.

The colouring matter itself was first isolated from the madder-root in 1827 by Colin and Robiquet, who obtained it by extracting ground madder with hot water and subliming the purified extract carefully in a glass tube.

This method of sublimation was not considered sufficient proof of the existence of alizarin in madder, and it was not till Schunck succeeded in isolating this substance by chemical means from the madder extracts used by dyers that this important point was definitely settled.

In assigning the correct formula to alizarin, considerable difference of opinion existed at first, owing no doubt to some extent to the difficulty experienced in obtaining alizarin in a condition pure enough for accurate analysis.

Schunck proposed the formula $C_{14}H_{10}O_4$, whilst Strecker believed it to be $C_{10}H_6O_3$ and related to 'chloroxynaphthalic acid' (chlorohydroxynaphthaquinone), a derivative of naphthalene, since both these substances on oxidation yield phthalic acid.

Strecker's formula was the more generally accepted by chemists, and chloroxynaphthalic acid was looked upon as being simply chlorinated alizarin, the two bodies being thus related:

$C_{10}H_6O_3$	$C_{10}H_5ClO_3$
Alizarin.	Chlorinated alizarin or Chloroxynaphthalic acid.

In order to prove the relation supposed to exist between these two substances, it was only necessary to replace the chlorine atom in chloroxynaphthalic acid by hydrogen, when alizarin should result.

This operation was eventually accomplished by Martius and Griess, who obtained thus a substance of the formula $C_{10}H_6O_3$, which was, however, not identical with alizarin, and was therefore supposed to be isomeric with it.

Some time after these experiments of Martius and Griess, Graebe commenced his research on quinones, the working out of which led not only to results which proved beyond a doubt what the chemical nature of alizarin really was, but also eventually resulted in the artificial production of this important colouring matter. In pursuing this investigation Graebe succeeded in preparing chloranil $C_6Cl_4O_2$, by treating phenol with potassium chlorate and hydrochloric acid, and in acting on this with caustic potash he found that two of the atoms of chlorine in this compound became replaced by (OK), producing the potash salt of chloranilic acid $C_6Cl_2(OK)_2O_2$, a change the knowledge of which proved to be of the utmost importance in his subsequent experiments on the artificial production of alizarin.

Chloroxynaphthalic acid was now considered by Graebe to be related to naphthalin in much the same way as chloranil was to benzene, *i.e.* to be a derivative of naphthaquinone.

Soon after this the attention of Graebe and Liebermann was turned to alizarin, which they also thought might belong to the quinone series.

In determining the constitution of this substance, the first step was to obtain some information as to the nature of the hydrocarbon from which alizarin was derived, and this was done in the following way: Alizarin prepared from madder was mixed with zinc-dust and heated strongly in a furnace, according to Baeyer's method of reducing benzenoid compounds, and in this way a crystalline hydrocarbon was obtained having the composition $C_{14}H_{10}$, which on examination was found to be identical with anthracene, a hydrocarbon previously obtained by Dumas and Laurent from coal tar. Using the information already obtained in the research on quinone, Graebe and Liebermann now assumed that alizarin must be a dihydroxyquinone of anthracene, the relation of these substances to one another being seen from the following formulæ:—

$C_{14}H_{10}$	$C_{14}H_8O_2$	$C_{14}H_6O_2(OH)_2$
Anthracene.	Anthraquinone.	Alizarin.

Having thus obtained anthracene from alizarin, it was now only necessary to reverse the operation and convert anthracene into alizarin, and the problem of the artificial production of a vegetable colouring matter would be solved for the first time.

In 1862 Anderson, while investigating anthracene, obtained from it by oxidation a substance of the formula $C_{14}H_8O_2$, which he named oxanthracene.

In this substance Graebe and Liebermann recognised the quinone of anthracene (anthraquinone), the first step in the synthesis of alizarin from anthracene, and in order to convert this quinone into alizarin all that was necessary was to replace two atoms of hydrogen in it by hydroxyl, an operation which is easily done in the following way:—

Anthraquinone when heated with two molecules of bromine in sealed tubes is converted into dibromanthraquinone, thus:

$$C_{14}H_8O_2+2Br_2=C_{14}H_6Br_2O_2+2HBr.$$

This substance when heated with potash exchanges each of its bromine atoms for (OK), yielding the potash salt of alizarin, $C_{14}H_6(OK)_2O_2$, a reaction which is precisely similar to the formation of chloranilate of potash from chloranil as described above. The potassium alizarate thus obtained, when decomposed with hydrochloric acid, yielded alizarin, and thus the problem of the artificial production of alizarin was solved.

In considering this synthesis, perhaps the most remarkable fact, from a chemical point of view, is that, in consideration of the number of possible isomers of alizarin, just that dibromanthraquinone prepared by Graebe and Liebermann should on treatment with potash have yielded alizarin. Had this not been so, the artificial production of alizarin would no doubt have been very much delayed.

The great importance of alizarin as a dyeing agent induced Graebe and Liebermann to patent this process, which proved, however, to be of no commercial value, owing to the great expense attending the use of bromine, and it was therefore desirable to find some new method which would render their discovery important from a manufacturing point of view.

This was first achieved by W. H. Perkin [1] in the following way:—Sulphuric acid, as is well known, forms with many organic bodies compounds called sulphonic acids, which in composition simply correspond to the substance acted on *plus* sulphuric anhydride.

Thus benzene C_6H_6 when treated with sulphuric acid yields benzenesulphonic acid $C_6H_5SO_3H$; naphthalene $C_{10}H_8$, naphthalenesulphonic acid $C_{10}H_7SO_3H$. When fused with caustic potash these sulphonic acids are split up into the potassium salt of the corresponding phenol and potassium sulphite, thus:

$$C_6H_5SO_3H+3KOH=C_6H_5OK+K_2SO_3+2H_2O.$$

Similarly disulphonic acids when fused with potash are converted into dihydric phenols, thus:

$$C_6H_4(SO_3H)_2+6KOH=C_6H_4\begin{matrix}OK\\OK\end{matrix}+K_2SO_3+4H_2O.$$

In this second example it will be seen that a body is formed which bears the same relation to benzene as alizarin does to anthraquinone, and it was therefore probable that if anthraquinone were subjected to a similar series of reactions, alizarin would result.

The great obstacle to carrying out this synthesis, in the first instance, was the remarkable stability of anthraquinone in general and particularly towards sulphuric acid, which is so great that it dissolves in moderately hot sulphuric acid without change, and crystallises out again in needles on cooling.

When, however, a mixture of anthraquinone and sulphuric acid was heated very strongly, combination did eventually take place, the product becoming perfectly soluble in water, the solution now containing mono- and disulphonic acids of anthraquinone.

After removing the excess of sulphuric acid from the new product, it was mixed with caustic potash, and heated to about 180°.

During the heating the melt became darker and darker in colour, and eventually almost black, and on dissolving this in water a rich purple solution was obtained which when acidified with dilute sulphuric acid gave a copious precipitate of alizarin.

The great obstacle to the preparation of alizarin—viz. the use of bromine—was thus removed, and, as the future has proved, a process had been obtained by which this colouring matter could be manufactured in quantity and at a price so cheap as entirely to supersede the old method of dyeing with the madder root.

Another process for the manufacture of artificial alizarin shortly afterwards discovered by W. H. Perkin, and largely used by him on a manufacturing scale, is the following:—

Anthracene is treated with chlorine and thus converted into a beautifully crystalline compound called dichloranthracene $C_{14}H_8Cl_2$.

This substance combines with Nordhausen sulphuric acid, forming a bright-green solution, which contains a sulphonic acid of dichloranthracene. When heated with sulphuric acid this substance undergoes a remarkable change, hydrochloric acid and sulphurous acid are evolved, and a disulphonic acid of anthraquinone formed, thus:

$$C_{14}H_6Cl_2(SO_3H)_2+H_2SO_4$$

Dichloranthracene-disulphonic acid.

$$=C_{14}H_6O_2(SO_3H)_2+2HCl+SO_2.$$

Anthraquinone disulphonic acid.

This anthraquinone disulphonic acid when fused with potash yields alizarin.

Alizarin and the other colouring matters of this class will not dye unprepared fabrics; these must first of all be mordanted.

The mordants used in this case consist of metallic hydroxides—*e.g.* of aluminium, iron, and chromium. Chloride of tin (tin crystals) is also extensively employed.

With alumina mordants alizarin produces shades of red and pink; with iron mordants, shades of black and purple; with chromium mordants, a dull purple; and with tin crystals a bright yellowish orange. These mordants may also be mixed and thus a large variety of different shades produced. A description of the method of application of these various mordants and the processes employed in dyeing with alizarin will be found in the article DYEING.

Since the first production of artificial alizarin on the large scale, the study of this substance and of the various colouring matters related to it has received a large amount of attention at the hands of chemists, the result being that a considerable number of derivatives of anthraquinone have been prepared and examined.

Most of these are either colouring matters themselves, or easily converted into such, several of them being obtained on the large scale in the manufacture of alizarin.

These derivatives may be divided under the following heads:—

(1) Sulphonic acids of anthraquinone.
(2) Monohydroxyanthraquinones.
(3) Dihydroxyanthraquinones.
(4) Trihydroxyanthraquinones.
(5) Higher hydroxylated anthraquinones.

In this article are also included the two dyeing matters, Galleïn and Cœruleïn, which although not actually anthracene derivatives, are very closely allied to them.

[1] It should be mentioned here that while these experiments were in progress, Caro, Graebe and Liebermann were investigating the same reaction in Germany.

Sulphonic acids of anthraquinone.

Anthraquinone α-sulphonic acid

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H_3\cdot SO_3H. \quad (1)$$

It is a remarkable instance of the influence of a catalyst that whilst anthraquinone ordinarily sulphonates in the 2- position, yet in the presence of quite small amounts of mercury the 1- position is exclusively attacked.

In preparing anthraquinone α-sulphonic acid, 100 pts. of anthraquinone are heated for three hours at 130° with 110 pts. of sulphuric acid containing 29 p.c. sulphuric anhydride, and 0·5 part of mercury.

The free acid is easily soluble in alcohol and water, its lead, barium, and strontium salts are very insoluble in hot water. The calcium salt is fairly soluble, but crystallises on heating the solution. The potassium salt occurs in glistening yellow leaflets.

The further sulphonation of the α acid in presence of mercury leads to the formation of 1 : 5- anthraquinone disulphonic acid, mixed with 1 : 8- and 1 : 7- acids. The same mixture is produced by the direct sulphonation of anthraquinone (100 parts) with 200 parts of sulphuric acid containing 40 p.c. sulphur trioxide, in the presence of mercury (1 part) at 160° for one hour. The mixture of acids is converted into calcium salt and fractionally crystallised. The calcium salt of the 1 : 8- acid is least soluble, the middle fraction is the largest and consists of 1 : 5- whilst the calcium salt of 1 : 7- is easily soluble.

Similarly it has been found that anthraquinone β-sulphonic acid (*see* below) is changed by sulphuric acid in presence of mercury to a mixture of 2 : 8- and 2 : 5- anthraquinone disulphonic acids (N.B. 2 : 8- is same as 1 : 7). It is strange that the direct sulphonation of anthraquinone in the presence of mercuric sulphate also yields the 2 : 8- disulphonic acid. The constitution of these sulphonic acids has been demonstrated by their conversion into the corresponding hydroxyanthraquinones by heating under pressure with milk of lime.

Literature.—Iljinsky (Ber. 36, 4194–4200); Schmidt (Ber. 37, 66–72).

Anthraquinone- 2 or β-sulphonic acid

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H_3(SO_3H).$$

This acid is formed together with a certain amount of anthraquinone disulphonic acid by heating anthraquinone with fuming sulphuric acid to 170° or with ordinary sulphuric acid to 250°–260°.

In preparing it a mixture of one part of fuming sulphuric acid (containing 40–50 p.c. anhydride) and 1–1¼ parts of anthraquinone is gradually heated to about 170° and kept at this temperature for eight or ten hours, the whole being well stirred during the operation.

The product thus formed consists chiefly of the monosulphonic acid together with a little disulphonic acid and unchanged anthraquinone. On diluting with water the anthraquinone separates out, and can easily be filtered off, leaving the sulphonic acids in solution. In order to separate the mono- from the disulphonic acid the clear filtrate is neutralised with carbonate of soda (or caustic soda). This causes the difficultly soluble sodium salt of anthraquinone monosulphonic acid to separate out, leaving the easily soluble salt of the disulphonic acid in solution.

The pasty mass obtained on neutralising with soda is thoroughly pressed, washed with a little water, and then if required pure recrystallised from this solvent. In this way a beautiful brilliant white scaly crystalline mass is obtained, which consists of pure sodium anthraquinone monosulphonate, the so-called 'silver salt' of the alizarin manufacturer.

The free acid obtained by the addition of an acid to the soda salt crystallises in plates. It is very easily soluble in cold water and alcohol, but almost insoluble in ether.

When fused with caustic soda, this acid (or rather its soda salt) gives first hydroxyanthraquinone $C_6H_4\begin{<}CO\\CO\end{>}C_6H_3OH$, and then alizarin; and, as will be shown later on, alizarin, when prepared on a manufacturing scale, is invariably formed from the monosulphonic acid of anthraquinone, not from the disulphonic acid as might be expected. The reason for this is that on fusing hydroxyanthraquinone with caustic soda, a continuous process of oxidation and reduction is carried on, the change being represented by the following equation :—

$$C_{14}H_7(ONa)O_2+NaOH+O$$

Sodium monohydroxyanthraquinonate.

$$=C_{14}H_6\begin{(}ONa\\ONa\end{)}O_2+OH_2$$

Sodium alizarate.

the oxygen being supplied at the expense of a part of the hydroxyanthraquinone which is thereby reduced to anthraquinone. On the large scale this reduction is prevented by the use of chlorate of potash in the fusion.

Literature.—Graebe and Liebermann (Annalen, 160, 131; 212, 44; Ber. 7, 805).

Anthraquinone disulphonic acids

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H_2(SO_3H)_2.$$

When anthraquinone is heated to a high temperature with 2 or 3 parts of ordinary or better fuming sulphuric acid, a mixture of α- and β-anthraquinone disulphonic acid is obtained, which can be separated by fractional crystallisation of the sodium salts.

Preparation.—1. A mixture of 10 kilos. of anthraquinone and 20 to 30 kilos. of fuming sulphuric acid is heated to a temperature of 160°–170° until a sample taken out is found to dissolve completely in water. The product is then heated another hour to convert any mono- into disulphonic acid, poured into water, neutralised with caustic soda, and evaporated.—2. 10 kilos. of anthraquinone, 12 kilos. of hydrogen sodium sulphate, and 40 kilos. of ordinary concentrated sulphuric acid are heated in pressure tubes for five or six hours to 260°, the product treated with water, and the acids converted into sodium salts as above.

In concentrating the solution of the sodium salt obtained by either of the above methods, the sodium salt of the α-acid crystallises out first, the more readily soluble salt of the β-acid remaining in the mother-liquors, and thus by

repeated recrystallisation, the two acids are easily separated from one another.

The free acids obtained by decomposing the salts by an acid are both readily soluble in alcohol and water, but insoluble in ether and benzene; the *α*-acid crystallises in small yellow crystals, the *β*-acid in beautiful yellow plates.

The salts of the *α*-acid are sparingly soluble in water and crystallise with difficulty; those of the *β*-acid are readily soluble and crystallise with the greatest ease.

Besides these two important acids, two other disulphonic acids of anthraquinone are known—viz. *χ*-anthraquinone disulphonic acid and *ρ*-anthraquinone disulphonic acid.

Literature.—Schultz (Chemie des Steinkohlentheers, 709, 712); Perkin (Chem. Soc. Trans. 1870, 133); Graebe and Liebermann (Annalen, 160, 134).

χ-Anthraquinone disulphonic acid. This acid is formed by treating sodium *α*-anthracene disulphonate with nitric acid. The sodium salt crystallises in yellow prisms, which are sparingly soluble in water. On fusing with potash this salt yields chrysazin $C_{14}H_6(OH)_2O_2$, hydroxychrysazin $C_{14}H_5(OH)_3O_2$, *m*-hydroxybenzoic acid, and salicylic acid.

Literature.—Liebermann and Dehnst (Ber. 12, 1288).

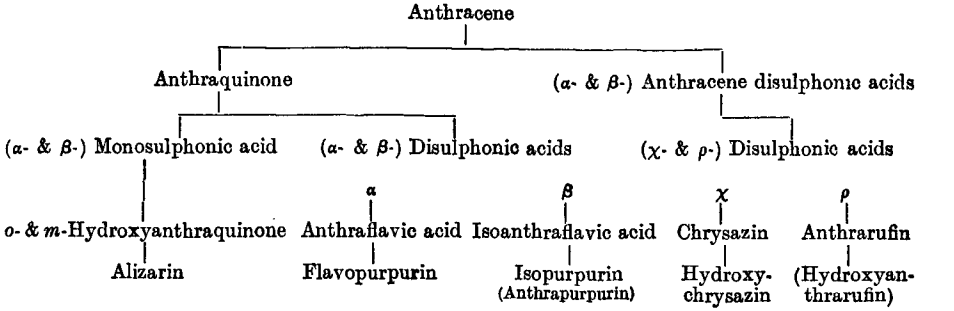
***ρ*-Anthraquinone disulphonic acid** is obtained by oxidising *β*-anthracene disulphonic acid. The soda salt crystallises in leather-yellow plates, which are easily soluble in water. On fusing with potash it yields anthrarufin

$$(OH)\cdot C_6H_3\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3(OH),$$

hydroxychrysazin $C_{14}H_5(OH)_3O_2$, *m*- and *o*-hydroxybenzoic acids.

Literature.—Liebermann and Dehnst (*l.c.*).

The relation of the various colouring matters of this group to anthracene, anthraquinone, and its sulphonic acids is easily understood from the following table (Schultz):—



The behaviour of the anthraquinone disulphonic acids on fusion with potash is exactly similar to that of the monosulphonic acid. Just as this acid on fusion with potash is first converted into monohydroxyanthraquinone and then by oxidation into dihydroxyanthraquinone (alizarin), so the anthraquinone disulphonic acids in the first place yield the corresponding dihydroxyanthraquinones, which then by the further action of the potash are converted into trihydroxyanthraquinones.

Hydroxyanthraquinones.

I. Monohydroxyanthraquinones

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3OH.$$

1- hydroxyanthraquinone. Erythroxyanthraquinone.

This substance is formed together with 2-hydroxyanthraquinone by strongly heating a mixture of phenol and phthalic anhydride with sulphuric acid

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle O + C_6H_5OH$$
$$= C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3(OH) + H_2O.$$

Also by heating 1- bromanthraquinone with potash to 160° or by acting on 1- amidoanthraquinone with nitrous acid in concentrated sulphuric acid solution.

1- hydroxyanthraquinone crystallises from alcohol in orange-red needles which melt at 190°. When fused with potash it gives alizarin. The substance does not dye mordanted fabrics.

1- Acetoxyanthraquinone, prepared by boiling erythroxyanthraquinone with acetic anhydride and sodium acetate, crystallises in yellow needles from alcohol and melts at 176°–179°.

1- methoxyanthraquinone is obtained by the action of boiling methyl alcoholic potash on 1- nitroanthraquinone.

This is the simplest example of a very general reaction in the anthraquinone series. The substance is yellow, microcrystalline, and melts at 140°–145°.

Literature.—Baeyer and Caro (Ber. 7, 969); Pechmann (Ber. 12, 2128); Römer (Ber. 15, 1793), Liebermann and Hagen (Ber. 15, 1804); Hoechste Farbwerke (D. R. P. 97688).

2- hydroxyanthraquinone.

This substance is obtained synthetically (together with erthroxyanthraquinone) by heating a mixture of phenol, phthalic anhydride, and sulphuric acid. The mixed hydroxyanthraquinones can be separated by means of baryta water, since the barium salt of 1- hydroxyanthraquinone is insoluble, whilst the 2- hydroxy compound is easily soluble. It crystallises from alcohol in yellow plates which melt at 323° and readily sublimes at a higher temperature.

It can be obtained in various ways from anthraquinone or its derivatives.

An easy preparation consists in melting anthraquinone sulphonic acid or 2- bromanthraquinone with potash.

The action of ammonium persulphate on a

solution of anthraquinone in concentrated sulphuric acid containing sulphur trioxide leads to the production of 2- hydroxyanthraquinone, alizarin, and purpurin.

Alizarin is reduced to 2- hydroxyanthraquinone by the action of alkaline stannous chloride; or alizarin amide, obtained by the action of ammonia on alizarin, yields this substance when treated with ethyl nitrite.

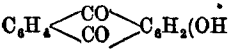
A very curious reaction of this hydroxyanthraquinone, and one which involves migration of an oxygen atom, is its conversion to quinizarin by treatment with nitrous acid in sulphuric acid solution and in the presence of boric acid.

Literature.—Graebe and Liebermann (Annalen, 160, 141); Baeyer and Caro (Ber. 7, 969); Liebermann and Fisher (Ber. 8, 975); Liebermann (Annalen, 183, 208); Wacker (J. Pr. Chem. [2] 54, 89); Bayer & Co. (D. R. P. 86830).

Dihydroxyanthraquinones.

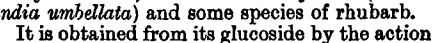
Alizarin

1 : 2- dihydroxyanthraquinone



Alizarin occurs in madder as the glucoside ruberythric acid, and also in Chay root (*Oldenlandia umbellata*) and some species of rhubarb.

It is obtained from its glucoside by the action of dilute acids or of ferments.



Ruberythric acid. Alizarin. Glucose.

It may be prepared artificially by many methods.

Thus alizarin is produced by fusing dichloranthraquinone, dibromanthraquinone, anthraquinone, mono- or di-sulphonic acids with potash. Rufigallic acid yields alizarin when reduced with sodium amalgam.

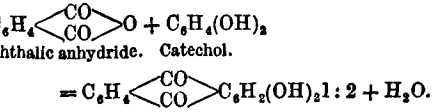
On the other hand, anthraquinone may be directly oxidised to alizarin by the action of ammonium persulphate in concentrated sulphuric acid solution.

Good yields of alizarin are said to be obtained by heating anthraquinone with sodium chlorate and a mixture of sodium and potassium hydroxides in aqueous solution at 200°. This process is used for the manufacture of alizarin, but it is not clear that it has entirely displaced the older process shortly to be described.

Hystazarin undergoes isomeric change to alizarin when heated with concentrated sulphuric acid to 200° for two and a half hours.

Alizarin may be synthesised by processes not involving the intermediate formation of anthraquinone.

Together with hystazarin it is produced when a mixture of catechol and phthalic anhydride is heated with sulphuric acid at 200°.

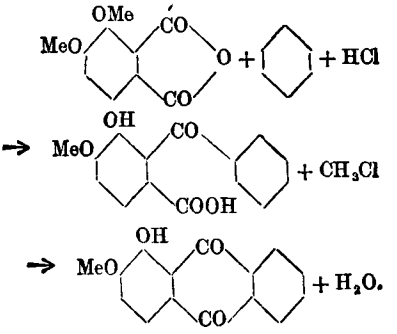


Phthalic anhydride. Catechol.

Alizarin.

Finally the following synthesis of alizarin is noteworthy :—

Hemipinic anhydride condenses with benzene in the presence of aluminium chloride, yielding the methyl ether of dihydroxybenzoylbenzoic acid. This latter substance, on treatment with hot sulphuric acid, is converted into alizarin methyl ether, which is hydrolysed by aluminium chloride to alizarin. The following formulæ represent this series of reactions :—



Alizarin methyl ether.

Manufacture of Alizarin.

1. *Anthraquinone process.*—Anthracene, the basis of alizarin, is obtained entirely from the coal-tar oils boiling above 300°, the so-called 'last runnings' of the tar distiller. These heavy oils are redistilled and the anthracene oils collected as soon as the distillate on cooling commences to solidify. In this way a semi-solid greenish-looking mass is obtained, which, after roughly freeing from excess of oil by treatment in hydraulic presses, is the starting-point in the alizarin factory. This crude product contains only about 30–40 p.c. anthracene, the remainder consisting of phenanthrene, naphthalene, carbazol, and small quantities of other hydrocarbons.

The first operation necessary in the manufacture of alizarin is that of purifying the crude anthracene obtained from the tar distillers, in order to obtain a product fit for the subsequent oxidation to anthraquinone.

This process of purification varies considerably in different countries, but the following method may be given as having been used with much success.

The crude anthracene is first ground between edge-runners, and then thoroughly agitated with boiling petroleum spirit in large iron vessels fitted with stirrers and heated with steam.

About 1500 to 1800 lbs. of crude anthracene and 300 gallons of petroleum spirit are used in one operation, the amount of the latter varying slightly according to the quality of the anthracene employed. After boiling for an hour or two, the product is allowed to cool, filtered through coarse canvas, and the anthracene on the filter washed with a little clean petroleum spirit. The pasty mass thus obtained is next treated with steam to remove the excess of petroleum spirit, and then sublimed. The sublimation process is best carried out by melting the anthracene in an iron pot, called the 'subliming pot,' and then blowing in superheated steam. This carries the anthracene vapour forward through a long pipe, where it meets a spray of water, which serves to condense both it and the steam.

The anthracene is thus obtained in an extremely finely divided state, much more suitable for oxidation than when simply ground under edge-runners as it used to be. The next step consists in converting the anthracene into anthraquinone by oxidation with bichromate of potash (or soda) and sulphuric acid—an operation which is usually done in the following way:—The anthracene is placed in lead-lined tanks with about twice its weight of the bichromate (dissolved in water), the requisite amount of dilute sulphuric acid is slowly added, and the mass kept well boiled and agitated by a steam jet connected with a Körting's injector.

The whole is then transferred to settling tanks, the crude yellowish-brown anthraquinone well washed by decantation until free from green chrome liquors, well drained, and freed from water as completely as possible by placing it in canvas bags and exposing it to great pressure in a hydraulic press. The amount of oxidiser required to convert the crude anthracene into anthraquinone is of course regulated by the purity of the sample employed, pure anthracene requiring about 1·66 times its weight of potassium bichromate to convert it into anthraquinone.

Instead of potassium bichromate, the sodium salt is now very often used on account of its cheapness.

The anthraquinone thus obtained is still very impure, and must be carefully purified before it can be converted into sulphonic acid. In purifying anthraquinone two methods may be employed:

(1) The anthraquinone is sublimed, and then recrystallised from high boiling coal-tar naphtha.

(2) The anthraquinone is treated with concentrated sulphuric acid.

When the first process is employed, the anthraquinone is melted in iron pots and subjected to the action of super-heated steam. The steam carries the vapour of the anthraquinone with it, and on condensation a fine, almost impalpable, powder is obtained, which, when dried and recrystallised from high-boiling coal-tar naphtha, consists of nearly pure anthraquinone.

In this country this process has now been almost abandoned; method (2) having entirely taken its place.

The working of this method is based on the fact that crude anthraquinone when treated with sulphuric acid at 100° dissolves, but is not acted on. The impurities, however, become converted into sulphonic acids, which, being easily soluble, can be removed by treating the product with water, when nearly pure anthraquinone is left behind.

In carrying out this operation a mixture of 1 part of crude anthraquinone and 3 parts of sulphuric acid is placed in large circular lead-lined iron pots, and heated by steam for twenty-four hours, the whole being continuously agitated by a stirrer.

The blackish-looking product is then run into shallow tanks, and exposed to the action of damp air, or a gentle current of steam, until the acid has become diluted. In a short time anthraquinone separates out as a light-brown crystalline powder, which, after washing by decantation, pressing, and thoroughly drying, is found to contain about 95 p.c. of pure substance.

According to recent patents anthraquinone is best purified by crystallisation from liquid sulphur dioxide or ammonia.

The anthraquinone is now in a condition suitable for conversion into the sulphonic acid.

This operation, which consists in heating anthraquinone with fuming sulphuric acid, is conducted in large iron pots capable of holding from 30 to 40 gallons. The amount of fuming sulphuric acid employed depends on the nature of the sulphonic acid required. In preparing the monosulphonic acid, 1 part of fuming acid (contained 40–50 p.c. SO_3) and 1 to 1½ parts of anthraquinone are used.

The mixture is gradually heated by means of an oil-bath to 170°, or even to 190°, and kept at this temperature for eight or ten hours, the stirrer being kept constantly in motion.

The product, which contains, besides anthraquinonemonosulphonic acid, a little disulphonic acid, and some unacted-on anthraquinone, is diluted with water, passed through a filter-press to remove the anthraquinone, and neutralised with caustic soda.

In a short time the whole becomes quite thick owing to the separation of the sparingly soluble soda salt of anthraquinonemonosulphonic acid, the easily soluble salts of the disulphonic acids remaining in solution.

The crystalline salt is collected in filter-presses, washed with a little very dilute sulphuric acid, and thus obtained practically pure in beautiful, brilliant, pearly scales.

In preparing the disulphonic acids of anthraquinone, the operation is similar to the above, the only difference being that more fuming sulphuric acid is used and the sulphonation conducted at a much higher temperature (about 260°).

The next operation consists in the conversion of the product just described, and called 'soda salt,' into colouring matter, a change which is accomplished by heating it strongly with caustic soda and a little potassium chlorate.

If the potassium chlorate is not added, a considerable loss is incurred owing to the reducing action of a large quantity of nascent hydrogen, always formed during the fusion, which converts the soda salt partially into anthraquinone and hydroanthraquinone. The fusion is conducted in large wrought-iron cylinders fitted with stirrers and heated with hot air. The usual charge is 700 lbs. caustic soda (70 p.c.) dissolved in water, 1300 lbs. of a concentrated solution of 'soda salt,' and 13 to 15 p.c. of potassium chlorate, the amount of this latter substance varying slightly with the nature of the salt used, the monosulphonic salt requiring more chlorate than the disulphonic salt.

The temperature is maintained at about 180° for at least twenty-four hours and often much longer, the progress of the decomposition being controlled from time to time by extracting small quantities of the melt and examining them in the laboratory.

The product thus obtained is an intense purple fluid, becoming thick on cooling and containing the colouring matter as sodium salt besides sodium sulphite and an excess of caustic soda.

To separate the colour the melt is run into large wooden tanks, diluted with water, and boiled with dilute sulphuric acid.

This causes the solution to become orange in colour owing to the precipitation of artificial alizarin.

After being allowed to settle, the supernatant liquor is run off, the alizarin forced into filter-presses and carefully washed until free from acid and saline matter. The colouring matter is then made up to a definite strength (10 p.c. or 20 p.c. paste as required) by transferring it to large wooden tubs fitted with powerful stirrers, and thoroughly mixing it with water.

Pure alizarin thus prepared produces a blue shade of Turkey-red, and anthrapurpurin (produced by fusing sodium anthraquinonedisulphonate with caustic soda) a red shade, so that by varying the amounts of these two constituents any intermediate shade required by the market can be obtained.

2. *Dichloranthracene process.*—In manufacturing alizarin by this process it is necessary, in the first place, to purify the anthracene used much more thoroughly than is the case in the anthraquinone process.

For this purpose the anthracene, after washing with petroleum spirit as described in the last process, is submitted to distillation with potash. This removes the carbazol and the phenolic substances present in the crude anthracene, and as, besides this, a considerable quantity of the other impurities are charred during the distillation, the anthracene resulting, although still very impure, is found to be greatly improved in quality.

In carrying out this operation 100 parts of washed anthracene, 30 parts of potash, and 6 parts of powdered lime are thoroughly ground together under edge-runners, the mixture introduced into iron retorts and distilled. The distillate, which consists of pale-yellow cakes containing about 50 p.c. of pure anthracene, is now sufficiently pure for conversion into dichloranthracene.

In chlorinating anthracene, leaden chambers are used, technically known as 'chlorine ovens.' These are 10 ft. long, 4 ft. 6 in. wide, and 1 ft. 6 in. deep, and are used in pairs, connected at one end in order that any chlorine escaping from the first oven may come in contact with a fresh amount of anthracene and thus prevent loss.

400 lbs. of anthracene are put into each oven, and subjected to the action of a rapid current of chlorine for about five or six hours.

The anthracene first fuses and gets dark in colour, hydrochloric acid being evolved in abundance; but after a time this fluid product begins to deposit crystals and soon becomes a semi-solid mass. In order to purify this crude product, it is first freed from hydrochloric acid by washing with dilute caustic soda, and then pressed between linen cloths in a hydraulic press, by which means a considerable quantity of a thick dark oily product, technically known as 'chlorine oils,' is got rid of.

The yellow cakes of dichloranthracene thus obtained are still not pure enough for use; they must next be soaked in coal-tar naphtha for some time and pressed, this operation being repeated until a product is obtained which contains 84 p.c. of pure substance.

The next process consists in converting the dichloranthracene into the sulpho- acids of anthraquinone by treating it with ordinary concentrated sulphuric acid. This decomposition is accomplished in iron pots capable of holding about 30 gallons and fitted with iron covers in which there is an opening for the escape of the acid vapours formed during the reaction.

These pots are charged with 350 lbs. of concentrated sulphuric acid and heated to 140°–160° by means of an ordinary fire, the dichloranthracene (70 lbs.) being shovelled in in small quantities at a time. After all the dichloranthracene has been added and the frothing due to the evolution of the hydrochloric and sulphurous acids produced during the decomposition has subsided, the temperature is gradually raised to 260° and then maintained at this point until a sample taken out on a glass rod and diluted with water forms a nearly clear solution devoid of fluorescence.

The product contains now the mono- and disulphonic acids of anthraquinone, the latter of which greatly predominates.

These crude sulphonic acids are next diluted with water in a large wooden tank and boiled with slaked lime until neutralised. The neutral product is then forced into filter presses to separate the calcium sulphate, the clear filtrate mixed with the washing of the calcium sulphate, evaporated until it contains about 15 p.c. of lime salts, and then treated with sufficient sodium carbonate to precipitate all the lime as carbonate.

The solution of the sodium salts of the sulphonic acids is siphoned from the precipitated calcium carbonate, concentrated until it contains 30 p.c. of soda salts, and then converted into colouring matter by fusion with caustic soda, as described in the last process.

Purification of artificial alizarin. Commercial alizarin contains as impurities hydroxyanthraquinone, anthrapurpurin, flavopurpurin, and small quantities of other colouring matters.

In order to separate the alizarin from these, the crude commercial product is dissolved in dilute caustic soda, and the solution treated with carbonic acid until two-thirds of the colouring matter has been precipitated as acid sodium salt. The precipitate is collected, washed with water, decomposed with hydrochloric acid, the crude alizarin thus obtained dissolved in caustic soda, and the treatment with carbonic acid repeated twice more.

The purified product is then boiled with baryta water to remove hydroxyanthraquinone and anthraflavic acid (which dissolve), the barium salt of alizarin is collected, washed, decomposed by hydrochloric acid, and the alizarin either sublimed or recrystallised from alcohol.

Another method of separation is based on the temperatures at which the various constituents of the mixture sublime. Alizarin itself sublimes at 110°, flavopurpurin and anthrapurpurin at 160° and 170° respectively.

Alizarin crystallises from alcohol in red needles or prisms, which melt at 282°. With care alizarin can be sublimed in magnificent deep-red prisms, which, if the operation be performed on a large scale, may be obtained over an inch in length.

It dissolves in alkalis with a purple colour, and is completely precipitated from this solution by the addition of lime or baryta in the form of a blue precipitate of the calcium or barium salt. Heated with acetic anhydride to 160° alizarin forms a diacetyl compound $C_{14}H_6O_2(C_2H_3O)_2O_2$,

which crystallises from alcohol in long yellow needles, melting at 160°. When treated with nitrous acid, alizarin yields anthraquinone. Nitric acid acts violently on alizarin with evolution of red vapours and formation of phthalic and oxalic acids. Distillation with zinc reduces alizarin to anthracene.

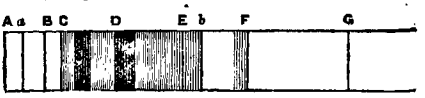
When fused with alkaline hydroxides at a fairly high temperature, protocatechuic acid and benzoic acid are formed. Concentrated aqueous ammonia at 200° replaces the hydroxyl in position (1) by amidogen. The 1-amido-2-hydroxyanthraquinone so produced is called alizarin amide.

Salts of alizarin. *Calcium alizarate*

$$CaC_{14}H_6O_4+H_2O$$

is precipitated by adding calcium chloride to an ammoniacal solution of alizarin as a purple mass. *Barium alizarate* $BaC_{14}H_6O_4+H_2O$ is prepared, like the calcium salt, by mixing an alkaline solution of alizarin with barium chloride. It is deep-violet when moist, almost black when dry, and very sparingly soluble in water. *Aluminium alizarate* $(C_{14}H_7O_2)_3Al_2O_3(?)$ is obtained by precipitating an alkaline solution of alizarin with alum or aluminium hydroxide. It is a very fine red or rose-red precipitate. *Lead alizarate* $C_{14}H_6O_4Pb$ is obtained by mixing an alcoholic solution of alizarin with an alcoholic solution of sugar of lead.

Alizarin can readily be detected by means of the spectroscope, as it gives in alkaline solution two sharp absorption bands, one at D and one near C, as will readily be seen from the accompanying figure, which shows the absorption



spectrum of a solution of alizarin in alcoholic potash.

Literature. — Anderson (J. 1847–48, 749); Stenhouse (J. 1864, 543); Rochleder (Ber. 3, 295); Perkin (Chem. Soc. Trans. 23, 141); Graebe and Liebermann (Annalen Suppl. 7, 300; Ber. 3, 359); Baeyer and Caro (Ber. 7, 972); Liebermann (Annalen, 183, 206); Liebermann and Dehnst (Ber. 12, 1293); Schunck (Annalen, 66, 187); Wolff and Strecker (Annalen, 75, 8); Lagodzinski (Ber. 28, 1428); Widman (Ber. 9, 856); Liebermann Hohenemser (Ber. 35, 1779); D. R. P. 116526; Perkin (Chem. Soc. Trans. 75, 453).

Derivatives of alizarin. When treated with the ordinary re-agents, such as bromine, nitric acid, &c., alizarin forms a variety of valuable substitution products, some of which are used to a considerable extent as dyeing agents. The most important of these are the following :—

Alizarin methyl ether

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H_2\begin{<}OH\ (1)\\OMe.\ (2)\end{>}$$

The synthesis of this substance from hemipinic acid has already been described (p. 78).

It can also be produced by treating the monopotassium salt of alizarin with methyl iodide or methyl sulphate.

The substance crystallises from alcohol, and has the melting-point 224°–226°.

The dimethyl ether is not obtained by acting on the potassium salt of the monomethyl ether with methyl iodide.

Alizarin diethyl ether

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H_2\begin{<}OEt\ (1)\\OEt.\ (2)\end{>}$$

can, however, be prepared by heating alizarin with potash and potassium ethyl sulphate at 160° (Habermann, Monatsh. 5, 228).

Monobromalizarin

$$C_6H_4\begin{<}CO\\CO\end{>}C_6HBr\begin{<}OH\ (1)\\OH.\ (2)\end{>}$$

This derivative can be prepared by heating alizarin with bromine and carbon disulphide to 180°–190° for four or five hours.

It is better prepared, however, by sulphonating alizarin with fuming sulphuric acid, and subsequently treating the solution with bromine.

It crystallises from glacial acetic acid in orange-coloured needles, which, when heated, first melt to an orange-coloured liquid and then sublime in orange-red needles.

As a dyeing agent, monobromalizarin retains all the properties of combining with mordants possessed by alizarin, and the colours produced appear to be equally fast. The shade of colour produced is, however, not the same, the reds being less purple, and the purples less blue than those produced by alizarin.

Literature.—Perkin (Chem. Soc. Trans. 27, 401).

α-Nitroalizarin. Alizarin brown

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H\begin{<}OH\ (1)\\OH\ (2)\\NO_2.\ (4)\end{>}$$

This substance is obtained by treating diacetyl alizarin with nitric acid.

It is manufactured by dissolving alizarin in fuming sulphuric acid and after cooling to −5° to −10°, treating with the calculated quantity of nitric acid dissolved in sulphuric acid.

α-Nitroalizarin crystallises from alcohol or glacial acetic acid in golden-yellow needles. It dissolves in caustic alkali with a blue-violet colour, but if only a minute quantity of alkali is employed the solution is of a fine crimson colour. The alkaline solution gives two absorption bands similar to alizarin. Nitroalizarin is easily reduced in alkaline solution with sodium amalgam or ammonium sulphide and amidoalizarin is the product.

On warming with sulphuric acid 1 : 2 : 3 : 4-tetrahydroxyanthraquinone is produced.

α-Amidoalizarin. Alizarin garnet, Alizarin cardinal

$$C_6H_4\begin{<}CO\\CO\end{>}C_6H\begin{<}OH\ (1)\\OH\ (2)\\NH_2.\ (4)\end{>}$$

This valuable dye-stuff is obtained by the reduction of α-nitroalizarin. It crystallises from alcohol in small needles of a nearly black colour, but possessing a slight greenish metallic reflection.

Its alcoholic solution gives two absorption bands; the first is a little beyond D and the second near C. There is also a faint line close to F.

Dyeing Properties of α-Nitro- and α-Amido-alizarin. These colouring matters possess the

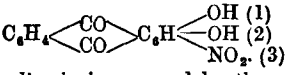
power of dyeing ordinary madder mordants. α-Nitroalizarin gives with alumina mordants very clear orange-red colours, not unlike some of the colours produced with aurin, and with iron mordants reddish-purple colours. Amidoalizarin gives with alumina mordants purple colours, and with iron a bluish or steel-like colour.

It is used for wool-dyeing and calico-printing.

Alizarin Maroon is a mixture of amidoalizarins and purpurins obtained by the reduction of the product of nitration of commercial alizarin in sulphuric acid solution. On alumina mordants it produces a garnet red, maroon on chrome.

Literature.—Perkin (Chem. Soc. Trans. 30, 578); Brasch (Ber. 24, 1610); Schunck and Römer (Ber. 12, 587); D. R. PP. 66811, 74431, 74598.

β-Nitroalizarin, Alizarin Orange



β-Nitroalizarin is prepared by the action of nitric acid on alizarin and also by boiling dinitro-2-hydroxyanthraquinone with caustic soda of 20 p.c.

It is manufactured in large quantities by the action of nitric acid on alizarin dissolved in sulphuric acid containing boric acid. The influence of the boric acid on the position attacked by the nitric acid is probably due to the formation of a boric ester of alizarin.

The crude β-nitroalizarin is purified by crystallisation from glacial acetic acid.

β-Nitroalizarin crystallises in orange-yellow needles which melt with decomposition at 244°. When carefully heated it sublimes, with a good deal of decomposition, in yellow needles. Dissolved in alkalis it forms a purple solution; the *sodium* salt is insoluble in an excess of caustic soda. The *calcium* salt is an insoluble violet-red precipitate, which is not decomposed by carbonic acid (distinction from alizarin). Treated with glycerol and sulphuric acid, β-nitroalizarin is converted into alizarin blue.

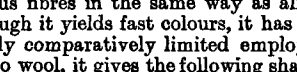
The diacetate of β-nitroalizarin crystallises in yellow needles melting at 218°.

β-Nitroalizarin is prepared on the large scale, and comes into the market under the name of 'Alizarin orange.' In dyeing it is applied to the various fibres in the same way as alizarin; but although it yields fast colours, it has as yet found only comparatively limited employment. Applied to wool, it gives the following shades:—

With an aluminium mordant it yields a very good orange; with stannous chloride mordant, a reddish or yellowish orange, according to the amount of mordant used; with copper sulphate mordant, a good reddish-brown is obtained; with ferrous sulphate, a purplish-brown; and with bichromate of potash, a dull brownish-red.

Literature.—Rosenstiehl (Bull. Soc. chim. 26, 63); Schunck and Römer (Ber. 12, 584); Simon (Ber. 15, 692); Bayer & Co. D. R. P. 74562.

Alizarin Red S

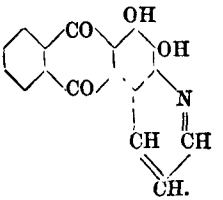


This dyestuff is the sodium salt of the monosulphonic acid of alizarin. It is easily prepared by the action of concentrated sulphuric acid on alizarin.

It yields brilliant scarlet red shades with an aluminium mordant, bordeaux red with chromium.

Literature.—Graebe and Liebermann (Annalen, 160, 144).

Alizarin Blue



This important colouring matter, discovered by Prud'homme, is obtained by treating β-nitroalizarin with glycerol and sulphuric acid or by treating β-amido alizarin with glycerol, nitrobenzene, and sulphuric acid. Its chemical constitution was first demonstrated by Graebe, who showed that this substance was related to alizarin in precisely the same way as quinoline is to benzene, *i.e.* that alizarin blue is a quinoline of alizarin.

Preparation.—1 part of β-nitroalizarin, 5 parts sulphuric acid, and 1½ glycerol (of sp.gr. 1·262) are mixed and gently heated.

At 107° the reaction commences and soon becomes very violent, the temperature rising to 200°. After the frothing has subsided, the mass is poured into water, the product well boiled, filtered, and the residue extracted three or four times with very dilute sulphuric acid. The combined extracts on cooling deposit the crude alizarin blue sulphate in brown crystals. These are collected, washed with water till neutral, mixed with water, and borax added until the solution becomes brownish-violet. The precipitate thus formed is filtered off, washed with water, and decomposed with a dilute acid, the crude alizarin blue thus obtained being purified by recrystallisation from benzene or glacial acetic acid.

Alizarin blue crystallises from benzene in brownish-violet needles which melt at 270°, and at a higher temperature gives off orange-red vapours which condense in the form of blue needles.

It is insoluble in water, sparingly soluble in alcohol and ether, more readily soluble in hot benzene. It dissolves in ammonia, potash, or soda, forming blue solutions which become green when mixed with an excess of alkali.

Alizarin blue combines with both bases and acids.

The barium salt $BaC_{17}H_7NO_4BaO+\frac{1}{2}H_2O$ is a greenish-blue precipitate. The following salts of alizarin blue with acids have been prepared:—

$C_{17}H_9NO_4,HCl$ is a red crystalline precipitate formed by passing dry hydrochloric acid gas through a solution of alizarin blue in boiling benzene. When treated with water it is completely decomposed into its constituents. The sulphate crystallises in red needles. The acetate $C_{17}H_9NO_4,C_2H_4O_2$ crystallises in blue plates.

Alizarin blue also combines with picric acid forming a compound $C_{17}H_9NO_4{\cdot}C_6H_3(NO_2)_3O$, which crystallises from benzene in long orange-

red prisms melting at 245°. This compound is completely decomposed by water. One of the most important compounds of alizarin blue is the sodium bisulphite compound

$$C_{17}H_9NO_4 \cdot 2NaHSO_3.$$

This product is manufactured on a large scale and sold under the name of 'Alizarin Blue S.' It dissolves readily in water, with a brownish-red colour. Alizarin blue is met with in commerce in two forms, viz. as a paste containing about 10 p.c. of dry substance, and as a powder. The former is nearly insoluble in water, while the latter, which is the bisulphite compound (described above), dissolves readily. This soluble kind is now almost entirely used in dyeing. In dyeing cotton with alizarin blue a chromium mordant is used, but in the case of wool, bichromate of potash gives the best results.

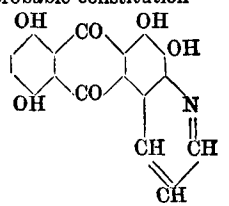
Alizarin blue with an alumina or iron mordant is also used for dyeing silk.

Alizarin blue is used largely as a substitute for indigo in calico-printing works. It is one of the most stable colouring matters, and is even said to be faster than indigo itself.

Literature.—Prud'homme (Bull. Soc. chim. 28, 62); Graebe (Annalen, 201, 333); Auerbach (Chem. Soc. Trans. 35, 800).

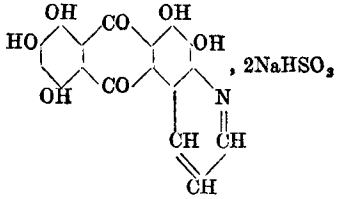
Alizarin Green S (B).

Alizarin blue can be oxidised by means of sulphur trioxide, and the product on treatment with sulphuric acid gives a dihydroxyalizarin blue of the probable constitution



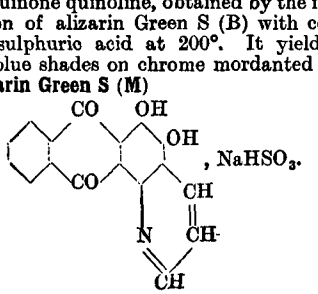
Alizarin Green S (B) is the bisulphite compound of this tetrahydroxyanthraquinone quinoline. It dyes very fast bluish-greens on chromed wool.

Alizarin Indigo Blue S



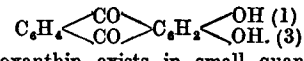
is the bisulphite compound of the pentahydroxyanthraquinone quinoline, obtained by the further oxidation of alizarin Green S (B) with concentrated sulphuric acid at 200°. It yields fast indigo blue shades on chrome mordanted wool.

Alizarin Green S (M)



This dyestuff is prepared from *a*-amidoalizarin by treatment with glycerol, nitrobenzene, and sulphuric acid. Its production and properties resemble those of alizarin blue. It is employed in printing, and is used with a nickel magnesia mordant.

Purpuroxanthin. 1 : 3-dihydroxyanthraquinone



Purpuroxanthin exists in small quantities in madder. It can be prepared by heating purpurin $C_{14}H_6(OH)_2O_2$ with iodide of phosphorus and water, or more readily by boiling purpurin with caustic soda and chloride of tin.

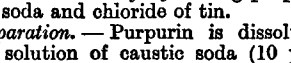
Preparation. — Purpurin is dissolved in a boiling solution of caustic soda (10 p.c.), and chloride of tin added until the solution loses its deep-red tint and becomes of a yellow colour. Hydrochloric acid is then added, the precipitate washed with strong hydrochloric acid, dissolved in baryta water, reprecipitated with hydrochloric acid and crystallised from alcohol.

Purpuroxanthin crystallises in reddish-yellow needles which melt at 262°–263°. It dissolves in alkalis with a reddish colour. If the solution in caustic potash be boiled in the air, it absorbs oxygen, the purpuroxanthin being reconverted into purpurin.

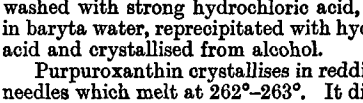
It is not a mordant dyestuff.

Literature.—Schützenberger and Schiffert (Bull. Soc. chim. 4, 12); Liebermann (Annalen, 183, 213); Schunck and Römer (Ber. 10, 172).

Quinizarin. 1 : 4-dihydroxyanthraquinone



is obtained by heating a mixture of quinol or *p*-chlorphenol and phthalic anhydride with sulphuric acid.



Together with alizarin and purpurin, it is obtained by the action of ammonium persulphate on anthraquinone in sulphuric acid solution; also on heating anthraquinone in sulphuric acid, containing boric acid, with nitrous fumes.

Preparation.—Equal parts of *p*-chlorphenol and phthalic anhydride are heated to 200°–210° for some hours, with ten times as much sulphuric acid as chlorphenol used. The product is poured into two or three times its volume of water, and after standing for twenty-four hours, the precipitate is filtered off, washed and pressed.

The crude product is then boiled with water to free it from phthalic acid, dissolved in caustic soda, precipitated with hydrochloric acid and recrystallised from alcohol. In order to remove a small quantity of purpurin, which is nearly always present, the crude quinizarin is then washed with cold dilute caustic soda as long as the solution is coloured red, and the residue recrystallised from toluene.

Quinizarin crystallises from alcohol in red needles which melt at 192°–193°, and sublime at a high temperature with partial decomposition. It dissolves readily in benzene. The solutions in ether and sulphuric acid are characterised by a beautiful greenish-yellow fluorescence. Quinizarin dissolves in baryta, forming a blue solution

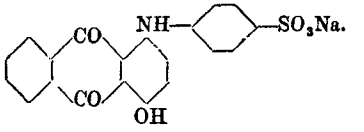
from which it is reprecipitated on passing carbonic acid (distinction from alizarin).

The tinctorial effects produced by quinizarin on fabrics mordanted with iron, chromium, or aluminium are about $\frac{1}{10}$ of those produced by an equal amount of alizarin.

When fused with potash it is converted into hydroxychrysazin $C_{14}H_8O_5$. Quinizarin forms a diacetate which melts at 200°.

Literature.—Baeyer and Caro (Ber. 8, 152); Schunck and Römer (Ber. 10, 554); Bayer & Co. D. R. P. 81245.

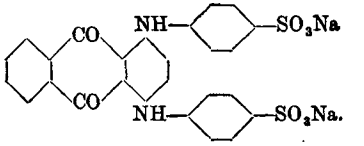
Quinizarin Blue



This dyestuff is prepared by heating quinizarin and aniline in molecular proportions and sulphonating the product. From an acid bath it dyes wool a red shade of blue, and gives a greenish blue with chromed wool.

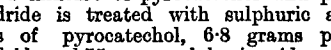
Quinizarin Green.

Quinizarin is treated with an excess of aniline and the product sulphonated. The dyestuff is the sodium salt of the sulphonic acid, and has the constitution



Toluidine and other amines may replace the aniline. The green shades produced on wool from an acid-bath are fast to light and milling.

Hystazarin. Hystazarin, 2 : 3-dihydroxyanthraquinone



This substance is formed, together with alizarin, when a mixture of pyrocatechol and phthalic anhydride is treated with sulphuric acid—5 grams of pyrocatechol, 6·8 grams phthalic anhydride and 75 grams sulphuric acid are heated for 4½ to 5 hours to 340–150° on a sand-bath.

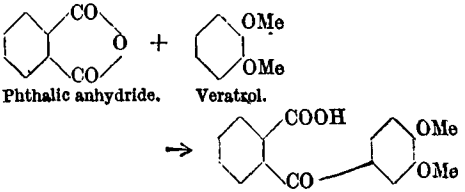
The resulting product, while still warm, is poured into ¾ litre of water, heated to boiling, and filtered hot.

The dark-green precipitate thus obtained is well washed with hot water, dissolved in dilute potash, and the dark-blue solution precipitated by dilute sulphuric acid. The precipitate is washed with water, dried on a porous plate, and treated with boiling alcohol in an extraction apparatus, by which means a considerable portion is dissolved.

The dark-red solution on evaporation yields an orange-red mass, which consists of alizarin and hystazarin. These two substances are readily separated by treatment with boiling benzene, which dissolves the alizarin and leaves the hystazarin; the latter may then be further purified by recrystallisation from acetone.

Yield 1½ p.c. alizarin and 12 p.c. hystazarin of pyrocatechol used.

Hystazarin may be synthesised by the following series of reactions:—Phthalic anhydride condenses with veratrol in carbon disulphide solution under the influence of aluminium chloride.



Phthalic anhydride. Veratrol.

3 : 4 : dimethoxybenzoylbenzoic acid.

The 3 : 4-dimethoxybenzoylbenzoic acid thus produced yields 2 : 3 : dimethoxyanthraquinone on heating with concentrated sulphuric acid. This is hystazarindimethyl ether and yields hystazarin on demethylation.

Hystazarin crystallises from acetone in orange-yellow needles, which do not melt at 260°.

It is almost insoluble in benzene, difficultly soluble in xylene, soluble in hot alcohol, ether, glacial acetic acid, and acetone.

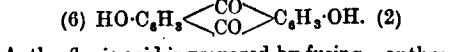
It dissolves in alkalis with a blue (cornflower) colour, in ammonia with a violet colour, and in concentrated sulphuric acid with a blood-red colour. The barium salt is a blue precipitate, the calcium salt a violet precipitate; both are insoluble in water.

Hystazarin possesses only very feeble tinctorial properties. The faint red colour produced with an aluminium mordant differs in shade from the alizarin red. The solution of hystazarin in dilute sodium hydrate absorbs the yellowish red and violet rays of the spectrum. A very dilute solution shows two lines in the yellow, $\lambda = 619{\cdot}8$, $\lambda_1 = 587{\cdot}4$. Distilled over zinc-dust, hystazarin yields large quantities of anthracene.

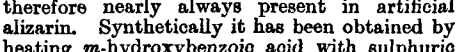
Diacetyl hystazarin $C_{14}H_6O_2(OC_2H_3O)_2$ crystallises from acetic acid in needles, which melt at 205°–207°.

Literature.— Liebermann and Schoeller (Ber. 21, 2501–2505); Lagodzinski and Lorétan (Ber. 28, 118).

Anthraflavic acid. 2 : 6-dihydroxyanthraquinone



Anthraflavic acid is prepared by fusing α-anthraquinone disulphonic acid with potash, and is therefore nearly always present in artificial alizarin. Synthetically it has been obtained by heating *m*-hydroxybenzoic acid with sulphuric acid to 190°.



This mode of formation proves that this substance contains the two hydroxyl groups in different benzene rings.

Anthraflavic acid crystallises from alcohol in yellow needles which melt above 330°. The pure substance when carefully heated sublimes partially in yellow needles, leaving a considerable quantity of a carbonaceous residue. Anthraflavic acid does not dye mordanted cloth. It dissolves in alkalis forming a yellowish-red solution, and in sulphuric acid forming a green solution, the

absorption spectrum of which shows a broad band between the blue and the green. Anthraflavic acid forms a number of salts, of which the sodium salt is the most characteristic. This salt is sparingly soluble in water, and is remarkable for the ease with which it crystallises; this distinguishes it from *iso*anthraflavic acid, and gives a ready means of separating these two substances. When treated with acetic anhydride, anthraflavic acid forms a diacetate melting at 228°–229°.

Literature.—Perkin (Chem. Soc. Trans. 1871, 24, 1109; 26, 19); Schunck and Römer (Ber. 9, 379; 11, 970); Liebermann (Ber. 5, 968); Rosenstiehl (Bull. Soc. chim. 29, 401–434); Barth and Senhofer (Ber. 170, 100).

***Iso*Anthraflavic acid.** 2 : 7-dihydroxyanthraquinone

(7) $HO{\cdot}C_6H_3\langle^{CO}_{CO}\rangle C_6H_3{\cdot}OH$ (2)

is formed when β-anthraquinone disulphonic acid is fused with potash, and is therefore always contained in crude alizarin. In preparing it, crude alizarin is dissolved in dilute caustic soda, the solution precipitated with hydrochloric acid, and the precipitate dissolved in cold baryta water and filtered. (In this way *iso*anthraflavic acid, which forms a soluble baryta compound, is easily separated from alizarin, anthrapurpurin, and anthraflavic acid, which yield insoluble barium compounds.) The filtrate is treated with hydrochloric acid, and the precipitate recrystallised from alcohol. *Iso*anthraflavic acid crystallises in long yellow needles, containing 1 mol. H_2O, which can be driven off at 150°. It melts above 330° and sublimes at a high temperature in lustrous yellow needles. It dissolves easily in alkalis forming a deep-red solution, but it does not dye mordanted cloth. Fused with potash *iso*anthraflavic acid yields anthrapurpurin.

The diacetate of *iso*anthraflavic acid melts at 195°.

Literature. — Schunck and Römer (Ber. 9, 379).

Anthrarufin. 1 : 5-dihydroxyanthraquinone

(5) $HO{\cdot}C_6H_3\langle^{CO}_{CO}\rangle C_6H_3{\cdot}OH$. (1)

Anthrarufin is formed together with anthraflavic acid and metabenzdioxyanthraquinone by heating *m*-oxybenzoic acid with sulphuric acid.

(2) $OH{\cdot}C_6H_4{\cdot}COOH$

$= OH{\cdot}C_6H_3\langle^{CO}_{CO}\rangle C_6H_3{\cdot}OH + 2H_2O.$

It may also be obtained by fusing *o*-anthraquinone disulphonic acid with potash.

The process employed for the manufacture of anthrarufin depends on the fact that it is the chief product when anthraquinone is oxidized with sulphur trioxide under the following conditions:—Anthraquinone (50 pts.) is heated with fuming sulphuric acid (1000 pts. containing 80 p.c. SO_3) and boric acid (20 pts.) for 36 hours at 100° under pressure.

Anthrarufin crystallises in yellow needles which melt at 280° and sublime easily at a higher temperature (distinction from anthraflavic acid). It dissolves with difficulty in ammonia and soda, but more readily in potash.

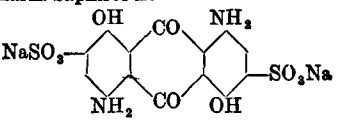
Anthrarufin dissolves in sulphuric acid, forming a deep-red solution, the colour of which is so intense that it is still easily apparent in solutions containing only 1 part in 10,000,000.

Anthrarufin forms a diacetate which melts at 244°–245°.

Anthrarufin dimethyl ether is obtained on boiling 1 : 5 : dinitroanthraquinone with methyl alcoholic caustic soda. The substance forms deep-red needles of m.p. 230°.

Literature.—Schunck and Römer (Ber. 11, 1175); Liebermann and Dehnst (Ber. 12, 1289); Bayer and Co. D. R. P. 101220.

Alizarin Saphirol B.



is an important blue acid wool-dye derived from anthrarufin by successive sulphonation, nitration, and reduction. This dyestuff excels in respect to its fastness to light.

Metabenzdioxyanthraquinone. 1 : 7 - dihydroxyanthraquinone

(7) $HO{-}C_6H_3\langle^{CO}_{CO}\rangle C_6H_3{-}OH$. (1)

Literature.—Schunck and Römer (Ber. 11, 1176); Liebermann and Dehnst (Ber. 12, 1289).

Metabenzdihydroxyanthraquinone $C_{14}H_8O_4$ is formed together with anthraflavic acid and anthrarufin by heating *m*-hydroxybenzoic acid with sulphuric acid (*v. supra*). It is separated from these by treatment with benzene and subsequent recrystallisation from dilute alcohol. Metabenzdihydroxyanthraquinone forms yellowish needles which melt at 291°–293°, and sublime at a higher temperature almost without decomposition. It dissolves in alkalis with a dark-yellow colour, and in concentrated sulphuric acid, forming a brownish-yellow solution, which shows no absorption bands.

The diacetate of metabenzdihydroxyanthraquinone melts at 199°.

Literature.—Schunck and Römer (Ber. 10, 1225); Rosenstiehl (Ber. 9, 946).

Chrysazin. 1 : 8- or 1 : 6-dihydroxyanthraquinone is formed by fusing χ-anthraquinone-disulphonic acid with potash, or by treating hydrochrysamid $C_{14}H_2(NH_2)_4(OH)_2O_2$ with nitrous acid and alcohol. (N.B.—Hydrochrysamid is obtained by the reduction of chrysammic acid $C_{14}H_4(NO_2)_4O_4$, which is the product of the action of nitric acid on aloes.)

Chrysazin forms reddish-brown needles, which melt at 191°. It dissolves in alkalis and sulphuric acid, with a red colour. Its diacetate melts at 227°–232°.

Crude dinitroanthraquinone contains a compound which is converted into chrysazin dimethyl ether on treatment with methyl alcoholic potash.

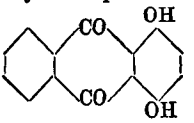
Literature.—Liebermann (Annalen, 183, 184).

***Iso*Chrysazin.** 1 : 6- or 1 : 8-dihydroxyanthraquinone has been obtained by Lifschütz, by treating dinitroanthraquinone with concentrated sulphuric acid. It crystallises from alcohol and ether in deep-red needles, which melt at 175°–180°. It dissolves in alkalis and in ammonia with a reddish violet colour, and in sulphuric acid with a reddish yellow colour. When heated it sublimes readily, and at a comparatively low temperature, in orange-red plates or needles. It does not dye mordanted cloth.

The *diacetyl compound* melts at 160–165°.

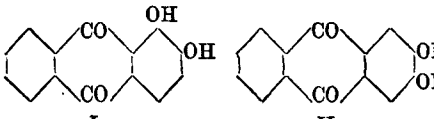
Literature.—Lifschütz (Ber. 17, 897).

Constitution of the dihydroxyanthraquinones. The synthesis of quinizarin from phthalic anhydride and quinol establishes its constitution as 1 : 4-dihydroxyanthraquinone



Further alizarin and hystazarin are produced by the condensation of phthalic anhydride with catechol.

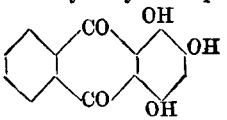
It follows that these colouring matters are represented by the following formulæ :—



I. II.

The synthesis of alizarin from hemipinic acid is conclusive evidence that the formula I. represents alizarin, and consequently II. is the structure of hystazarin.

Again, purpurin is produced by the oxidation of both alizarin and quinizarin, and must therefore be 1 : 2 : 4-trihydroxyanthraquinone



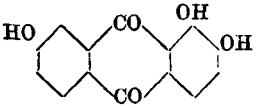
On reduction it yields neither alizarin nor quinizarin, but purpuroxanthin, which is obviously 2 : 4-dihydroxyanthraquinone (the same position as 1 : 3).

Similar arguments can be developed with respect to anthraflavic acid, *iso*anthraflavic acid, anthrarufin, and metabenzdioxyanthraquinone.

There remains a doubt as to the constitution of chrysazin and *iso*chrysazin, but it is most probable that chrysazin is 1 : 8-dihydroxyanthraquinone, in which case the hydroxyl groups in *iso*chrysazin must be in the 1 : 6 position.

The properties of chrysazin are similar to those of anthrarufin, and it is much more probable that dinitroanthraquinone is a mixture of 1 : 8 and 1 : 5 than of 1 : 6 and 1 : 5.

Trihydroxyanthraquinones : Anthrapurpurin, *Iso*purpurin, Hydroxy*iso*anthraflavic acid. 1 : 2 : 7-trihydroxyanthraquinone



This important colouring matter is contained in crude artificial alizarin. It is formed by fusing β-anthraquinonedisulphonic acid, *iso*anthraflavic acid, metabenzdihydroxyanthraquinone, or α-dibromanthraquinone with potash.

The preparation of this substance is a somewhat tedious process, dependent on the fact that anthrapurpurin differs from alizarin in the behaviour of its alumina lake. The former, on treatment with an alkaline carbonate, is dissolved, whilst the alizarin lake remains unattacked. The solution containing the anthrapurpurin is filtered from the alizarin lake, heated to boiling, and acidified with hydrochloric acid. The anthrapurpurin thus obtained is purified by conversion into its difficultly soluble sodium compound, and from this, by precipitation with barium chloride, the barium salt is obtained, which is decomposed with hydrochloric acid. The precipitate is collected on a filter, well washed with water and recrystallised from glacial acetic acid.

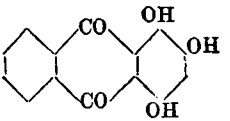
Anthrapurpurin crystallises in orange-coloured needles, which melt above 330°, and, when carefully heated, sublime in long red needles. It dissolves in alkalis with a violet colour; the solution shows the same absorption spectrum as alizarin.

With acetic anhydride anthrapurpurin forms a triacetate $C_{14}H_5(C_2H_3O)_3O_5$, which crystallises in yellow needles, melting at 220°. When heated with ammonia, anthrapurpurin is converted into anthrapurpurinamide $C_{14}H_5(NH_2)(OH)_2O_2$.

Anthrapurpurin has the same affinity for mordants as alizarin; the colours it produces are also analogous to some extent, as it produces reds with alumina, purples and blacks with iron mordants. There is, however, a considerable difference in the shade of colour produced, the reds being much purer and less blue than those of alizarin, whilst the purples are bluer and the blacks more intense. When used in Turkey-red dyeing it produces very brilliant colours of a scarlet shade, which are of remarkable permanence.

Literature.—Perkin (Chem. Soc. Trans. 25, 659; 26, 425; 29, 851); Caro (Ber. 9, 682); Schunck and Römer (Ber. 9, 679; 10, 972, 1823; 13, 42); Rosenstiehl (Bull. Soc. chim. 29, 405); Auerbach (J. 1874, 488).

Purpurin 1 : 2 : 4-trihydroxyanthraquinone



Purpurin occurs along with alizarin in madder, probably as a glucoside. In order to separate it from alizarin, the mixture of the two substances is repeatedly recrystallised from a hot solution of alum, in which purpurin is more soluble than alizarin, or the mixture is dissolved in caustic soda and the solution saturated with carbonic acid. This precipitates the alizarin, but not the purpurin.

Purpurin is obtained when alizarin or quinizarin (1 pt.) is heated with pyrolusite (1 pt.) and concentrated sulphuric acid (8–10 pts.) at 160°. The oxidation of alizarin to purpurin is also effected by the action of ammonium persulphate in sulphuric acid containing sulphuric anhydride. α-Amidoalizarin is changed to purpurin by the action of nitrous acid in sulphuric acid solution.

Purpurin crystallises from dilute alcohol in long orange-coloured needles, which contain 1 mol. H_2O. The pure substance begins to sublime at 150°, and melts at 253°. It is slightly soluble in water, forming a deep yellow solution; in alkalis it dissolves with a purple-red colour; in alkaline carbonates with a red colour. The solution in alkalis shows two marked absorption bands in the green. Purpurin also dissolves readily in ether, carbon disulphide,

benzene, and acetic acid; these solutions give two absorption bands, one at F and the other near E; the solution in sulphuric acid shows another line in the yellow. When boiled with acetic anhydride it yields a triacetate,

$$C_{14}H_5(C_2H_3O)_3O_5,$$

which crystallises in yellow needles, melting at 192°–193°.

Aqueous ammonia at 150° converts purpurin into purpurinamide

$$C_6H_4\begin{matrix}CO\\CO\end{matrix}C_6H(NH_2)(OH)_2 \quad (OH:OH:NH_2 = 1:3:4),$$

which, when boiled with ethyl nitrite, yields purpuroxanthin,

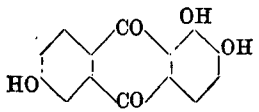
$$C_6H_4\begin{matrix}CO\\CO\end{matrix}C_6H_2\begin{matrix}OH\ (1)\\OH.\ (3)\end{matrix}$$

Purpuroxanthin is also the product when purpurin is reduced with either alkaline stannous chloride or sodium amalgam. If, however, zinc-dust be employed as the reducing agent in weakly alkaline, neutral, or acid solution, then the leuco- compound of quinizarin is obtained. Purpurin is converted into 2-anilino-1:4-dihydroxyanthraquinone when heated with a mixture of aniline and aniline hydrochloride. A certain amount of dianilino-hydroxyanthraquinone is produced at the same time.

Purpurin dyes fabrics much in the same way as alizarin and anthrapurpurin, there being, however, a difference in the shades. The reds produced by purpurin are much yellower, and the browns (with chrome mordant) much more intense than are produced either by alizarin or anthrapurpurin.

The following figure shows the absorption spectrum of a solution of purpurin in aluminium sulphate:—

Flavopurpurin. 1:2:6-trihydroxyanthraquinone

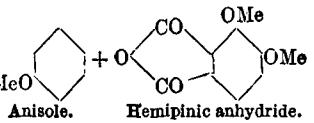


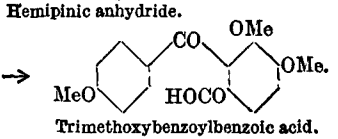
Flavopurpurin occurs in commercial artificial alizarin, but is with difficulty isolated from this product, owing to the fact that its chemical properties agree so closely with those of anthrapurpurin, which is also nearly always present in artificial alizarin, that it can only with difficulty be separated from this substance.

It is prepared by fusing β-anthraquinone-disulphonic acid or anthraflavic acid with potash.

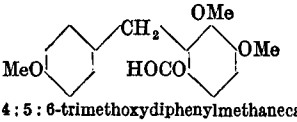
It may be synthesised by the following series of reactions:—

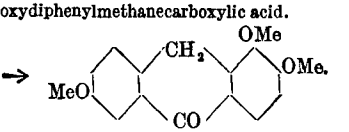
Hemipinic anhydride condenses with anisole in the presence of anhydrous aluminium trichloride, yielding the trimethyl ether of 4:5:6-trihydroxybenzoyl benzoic acid.





This benzophenone derivative is reduced by zinc-dust and concentrated hydrochloric acid, and the product is 4:5:6-trimethoxydiphenylmethanecarboxylic acid, which is changed by sulphuric acid to 1:2:6-trimethoxyanthrone.





1:2:6-trimethoxyanthrone crystallises from benzene in small needles melting at 170°. It is oxidised by chromic acid in glacial acetic acid solution to the trimethyl ether of flavopurpurin, which consists of yellow needles, crystallises from acetic acid, and melts at 225°. The trimethyl ether is hydrolysed to flavopurpurin by the action of aluminium chloride at 210°.

Flavopurpurin crystallises from alcohol in anhydrous yellow needles, sparingly soluble in water, but readily soluble in cold alcohol. Its melting-point lies above 330°.

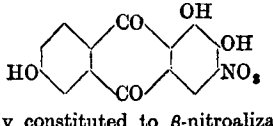
It dissolves in caustic alkalis with a purple colour; the solution shows two absorption bands, one in the blue and the other near the red, but a little further removed than the alizarin band.

Flavopurpurin dyes mordanted fabrics similarly to alizarin, there being, however, a slight difference in the shades produced. The red shade is somewhat duller and yellower; the brown shade is also yellower. Flavopurpurin dyes wool mordanted with tin crystals and cream of tartar a bright yellowish orange.

When heated with acetic anhydride, flavopurpurin yields a triacetate $C_{14}H_5(C_2H_3O)_3O_5$, which crystallises from alcohol in golden-yellow plates melting at 238°.

Alizarin Red 3 W. S. is the sodium salt of the monosulphonic acid of flavopurpurin.

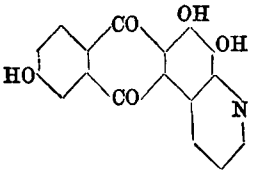
Alizarin Orange G. Nitroflavopurpurin



is similarly constituted to β-nitroalizarine. It is obtained by the nitration of flavopurpurin with ordinary nitric acid. Fast orange shades can be produced by applying this compound with an aluminium mordant.

On treatment with glycerol and sulphuric

acid a trihydroxyanthraquinone quinoline of the constitution

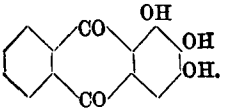


is produced, the bisulphite compound of which is the dyestuff **Alizarin Black P.**

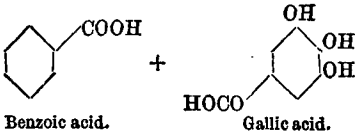
It is used for producing a fast violet grey to black in cotton-printing.

Literature.—Caro (Ber. 9, 682); Schunck and Römer (Ber. 9, 679; 10, 1823; 13, 42): Bistrzycki and Yssel de Schepper (Ber. 31, 2798).

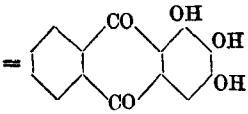
Anthragallol. 1 : 2 : 3-trihydroxyanthraquinone



Anthragallol does not itself occur in nature, but its three isomeric dimethyl ethers have been found in Chay root (*Oldenlandia umbellata*). Anthragallol is formed when a mixture of gallic acid (1 pt.), benzoic acid (2 pts.), and sulphuric acid (20 pts.) are heated to 125° for eight hours.



Benzoic acid. Gallic acid.



Anthragallol.

The product is poured into water, well washed, and recrystallised from alcohol.

It is also obtained from 1 : 3-dinitro-2-hydroxyanthraquinone (the nitration product of 2-hydroxyanthraquinone) by reduction in strongly alkaline solution. Or 1 : 3-diamido-2-hydroxyanthraquinone may be converted to anthragallol by heating with hydrochloric acid under pressure.

Anthragallol crystallises in yellow needles which, when heated to 290°, sublime without melting. It is sparingly soluble in water, chloroform, or carbon disulphide; readily soluble in alcohol, ether, or glacial acetic acid.

It dissolves in alkalis forming a green solution. Its triacetate $C_{14}H_5(C_2H_3O)_3O_5$ melts at 171°–173°.

With an excess of ammonia anthragallol reacts, forming anthragallolamide, 1-amido-2 : 3-dihydroxyanthraquinone.

Literature.—Seuberlich (Ber. 10, 39).

Hydroxyanthrarufin (Hydroxychrysazin).

1 : 4 : 5-trihydroxyanthraquinone. This substance is formed by fusing chrysazin, anthrarufin, ρ- or χ-anthraquinonedisulphonic acids with potash. It crystallises in small red needles, which are sparingly soluble in alcohol. When strongly heated it sublimes in red needles. It dissolves in potash, forming a violet solution, and shows in its reactions great similarity to purpurin. It differs from this substance in the fact that its solution in alum gives no absorption spectrum.

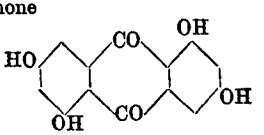
The solution in sulphuric acid shows, however, two weak bands. The substance is a mordant dyestuff.

The triacetate of hydroxyanthrarufin melts at 192°–193°.

Literature.—Liebermann (Annalen, 183, 191); Schunck and Römer (Ber. 11, 1179); Liebermann and Boeck (Ber. 11, 1617); Liebermann and Dehnst (Ber. 12, 1289).

Tetrahydroxyanthraquinones.

Anthrachrysone. 1 : 3 : 5 : 7-tetrahydroxyanthraquinone



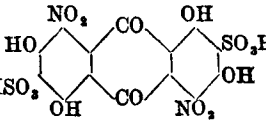
The preparation of this body is effected by heating 3 : 5-dihydroxybenzoic acid with 10 parts of sulphuric acid for 3 to 5 hours.

The substance consists of silky yellow needles when crystallised from alcohol, or it can be sublimed with partial decomposition in leaflets. It does not melt at 360°.

Anthrachrysone has a very feeble affinity for mordants. Its tetraacetate crystallises in yellow needles from acetic acid, and melts at 253°.

Various dyestuffs are derived from anthrachrysone.

Dinitroanthrachrysonedisulphonic acid



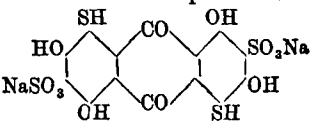
is prepared by sulphonation, followed by nitration of anthrachrysone.

It is a fast brown wool dye.

On reduction it yields diamidoanthrachrysonedisulphonic acid, which dyes wool violet from an acid-bath, or blue on a chromium mordant.

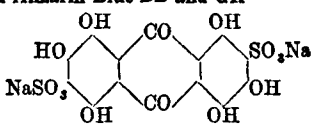
If, however, the reduction is carried out in alkaline solution with sodium sulphide, then the dyestuff **Acid Alizarin Green B and G** results.

The constitution of this product is



It dyes chromed wool a fast, pure green.

Acid Alizarin Blue BB and GR



is obtained by boiling diamidoanthrachrysonedisulphonic acid with alkali. A red shade is produced on wool from an acid-bath, which on

chroming develops a beautiful blue, exceedingly fast to light milling, acids or alkalis.

Literature.—Hohenemer (Ber. 35, 2305); Barth Senhofer (Annalen, 164, 109); Noah (Ber. 19, 755).

Rufiopin.

This tetrahydroxyanthraquinone is obtained by heating opianic or hemipinic acids with sulphuric acid at 180°.

Also by fusing the disulphonic acid of anthrarufin with potash.

It forms a reddish yellow crust from ether, and can be sublimed in orange needles.

It gives a violet-red solution in dilute alkalis or in sulphuric acid. A curious property of rufiopin is its stability towards fusion with potash.

The substance is of no value as a dyestuff, since it gives only dull-brown shades with mordants.

Literature.—Liebermann and Chojnacki (Annalen, 162, 323); D. R. P. 103988.

α- and β-hydroxyanthragallol.

A mixture of these substances is produced when equimolecular proportions of gallic and *m*-hydroxybenzoic acids are heated at 150°, with 10 parts of sulphuric acid for twenty hours.

The product is poured into water and the dried precipitate extracted with alcohol. This extract is evaporated and the residue treated with hot benzene. The α- compound passes into solution, whilst the β- remains undissolved.

α-hydroxyanthragallol crystallises from alcohol in golden yellow micro- needles. It forms a green solution in alkalis, whilst that in sulphuric acid is violet, and shows two absorption bands between F and D. With mordants it behaves similarly to rufigallic acid.

Its tetraacetyl derivative melts at 207°–209°.

β-hydroxyanthragallol crystallises from alcohol and occurs in red needles. Its brown-red solution in sulphuric acid shows two absorption bands between E and H.

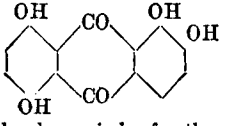
The tetra-acetate crystallises from glacial acetic acid in lemon-yellow tablets of m.p. 189°.

Literature.—Noah (Annalen, 241, 270).

1 : 2 : 3 : 4-tetrahydroxyanthraquinone is obtained by heating anthragallol with sulphuric acid in the presence of boric acid at 200°–240°. It consists of green needles soluble in both alkalis and sulphuric acid with red colour. The tetraacetyl derivative melts at 205°.

Literature.—Bayer and Co. D. R. P. 86968.

Alizarin bordeaux (Quinalizarin). **1 : 2 : 5 : 8-tetrahydroxyanthraquinone**



Alizarin bordeaux is by far the most important of the tetrahydroxyanthraquinones.

It has been obtained by the hydrolysis of its dimethyl ether (*see* below) with a solution of hydrochloric acid in acetic acid at 200°.

It is prepared by heating alizarin (1 pt.) with sulphuric acid (10 pts. containing 80 p.c. SO_3) for four days at 25°–50°. This yields the sulphuric acid ester of alizarin bordeaux, to obtain which the reaction product is rendered alkaline and then boiled with an excess of hydrochloric acid.

It is found that the oxidation of alizarin occurs more readily in presence of boric acid.

Alizarin bordeaux can be obtained in deep red needles with green metallic reflection.

On an aluminium mordant it produces bordeaux shades; violet blue on chromium.

The tetraacetate crystallises from chloroform-alcohol in micro- needles of m.p. 201°.

Dimethyl ether of alizarin bordeaux.

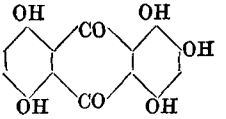
This substance is synthesised by heating hemipinic acid and quinol with sulphuric acid to 130°.

The brown-red micro leaflets obtained by crystallisation from benzene melt at 225°–230°.

Literature.—Schmidt (J. pr. Chem. [2] 43, 239); Liebermann and Wense (Annalen, 240, 299).

Pentahydroxyanthraquinones.

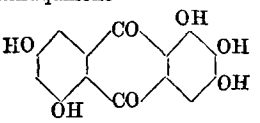
Alizarin cyanine R. **1 : 2 : 4 : 5 : 8-pentahydroxyanthraquinone**



This valuable substance is obtained by the oxidation of alizarin bordeaux with pyrolusite in sulphuric acid solution. The sulphonic acid ether so produced is hydrolysed by boiling with dilute acid. This oxidation is entirely analogous to that by which purpurin is produced from alizarin. The substance crystallises in bronze-coloured leaflets from nitrobenzene. The blue solution in concentrated sulphuric acid exhibits red fluorescence.

Alizarin cyanine R. yields a handsome blue chromium lake.

Dihydroxyanthragallol. **1 : 2 : 3 : 5 : 7-pentahydroxyanthraquinone**



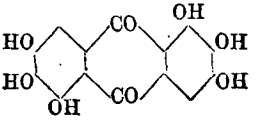
Equimolecular amounts of gallic acid and 3 : 5-dihydroxybenzoic acid are heated to 160° for ten minutes with ten times their weight of sulphuric acid. The product contains dihydroxyanthragallol, rufigallic acid, and anthrachrysone. In order to separate them, advantage is taken of the fact that only dihydroxyanthragallol pentaacetate is soluble in alcohol. The acetate so obtained is hydrolysed with cold sulphuric acid.

Dihydroxyanthragallol crystallises from alcohol in small red needles, which do not melt at 360°. The substance is similar in tinctorial properties to rufigallic acid.

The pentaacetate melts at 229°.

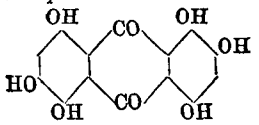
Literature.—Noah (Annalen, 241, 275).

Hexahydroxyanthraquinones. Rufigallol. Rufigallic acid, **1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone**



Rufigallic acid is produced when gallic acid is heated with concentrated sulphuric acid at 140°. It may be sublimed in yellow needles. A violet solution is obtained with alkalis, red with sulphuric acid. Baryta produces a blue insoluble precipitate. Alizarin is obtained by the reduction of rufigallic acid with sodium amalgam. The substance is a good example of a polygenetic dyestuff, and yields with aluminium, iron, and chromium mordants, red, violet, and brown respectively. The colours are, however, not pure in tone.

Anthracene Blue. 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone



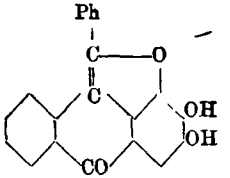
Anthracene blue is an important dyestuff, and can be obtained from erythroxyanthraquinone, anthrarufin, or anthrachrysone, by the oxidising action of sulphur trioxide in sulphuric acid in the presence of boric acid.

It is best prepared by the action of 40 p.c. sulphuric anhydride on 1 : 5-dinitroanthraquinone, and treatment of the product with ordinary sulphuric acid.

The solution in concentrated sulphuric acid is violet-blue and shows a brown fluorescence. The aluminium lake is violet and the chromium lake blue.

Its disulphonic acid is Acid alizarin blue B B, mentioned above, and prepared from anthrachrysone.

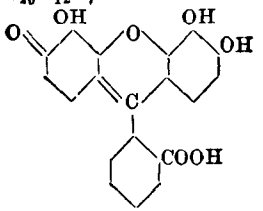
Benzoin Yellow



is prepared by the condensation of benzoïn with gallic acid under the influence of sulphuric acid.

It dyes wool on a chromium mordant a fast yellow (except to light).

Gallein $C_{20}H_{12}O_7$



Galleïn is formed by heating pyrogallol with phthalic anhydride.

Preparation.—A mixture of 1 part of phthalic anhydride and 2 parts of pyrogallol are heated to 190°–200°, the product dissolved in alcohol, and the colouring matter precipitated by the addition of water. The crude galleïn thus obtained is dissolved in alcohol, reprecipitated with water, and, after repeating this operation a few times, converted into the acetate by heating with acetic anhydride. This is recrystallised several times, and decomposed with potash.

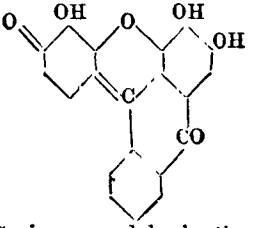
Galleïn crystallises from alcohol in small greenish crystals. It is insoluble in chloroform and benzene, sparingly soluble in water and ether, readily soluble in alcohol, forming a dark-red solution. It dissolves in cold concentrated sulphuric acid without change; on warming the solution cœruleïn is formed.

Galleïn dissolves in small quantities of potash or soda with a red colour; excess of alkali produces a blue solution. Heated to 150° with acetic anhydride galleïn yields a tetracetate of hydrogalleïn.

Galleïn (often called anthracene violet) is sold in the form of a reddish-brown powder, or a 10 p.c. paste; not very soluble in cold water, but readily so in hot. With all the usual alizarin mordants galleïn produces purple colours, which are fast to light and soap; those obtained by the use of chromium and iron are bluish, those with tin reddish, those with aluminium intermediate in tone.

Literature.—Baeyer (Ber. 4, 457 and 663); Buchka (Annalen, 209, 261); Orndorff and Brewer (Amer. Chem. J. 1901, 97).

Cœrulein $C_{20}H_{10}O_6$



Cœruleïn is prepared by heating 1 part of galleïn and 20 parts of sulphuric acid to 200°, and precipitating the colouring matter by adding a large quantity of water. It is thus obtained as a bluish-black mass, which, when rubbed, acquires a metallic appearance. It is almost insoluble in water, ether, and alcohol, more readily soluble in acetic acid.

It dissolves in alkalis with a green colour, in acids with an olive-brown colour. With bisulphite of soda cœruleïn forms an easily soluble compound. With acetic anhydride it forms a triacetate. Cœruleïn (anthracene green) is sold in two forms, either as a bluish-black paste containing 10–20 p.c. cœruleïn, or as a black powder.

The former is insoluble in water, the latter, known as cœruleïn S, is soluble in water, and is indeed a bisulphite compound of cœruleïn.

Cœruleïn is mostly employed in calico-printing for producing very fast olive-green shades. Whatever the mordant used, only different shades of olive-green are produced.

Literature.—Baeyer (Ber. 4, 556, 663); Orndorff and Brewer (Amer. Chem. J. 1901, 97).

W. H. P. and R. R.

ALIZARIN (Natural) *v.* CHAY ROOT and MADDER.

ALIZARIN AND METHYL ETHER *v.* CHAY ROOT.

ALIZARIN BLACK, -BLUE, -BORDEAUX, BROWN, -CARDINAL, -CYANINE, -GARNET, GREENS, -MAROON, -ORANGE, -REDS, -SAPHIROL *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ALIZARIN YELLOW *v.* AZO- COLOURING MATTERS.

ALIZARIN YELLOW A *v.* KETONES.

ALKALI ALBUMIN *v.* PROTEINS.

ALKALI BLUE. *Nicholson's blue. Sodium triphenyl-rosaniline sulphonate* (*v.* TRIPHENYL METHANE COLOURING MATTERS).

ALKALI BROWNS, -YELLOW *v.* AZO- COLOURING MATTERS.

ALKALIMETRY *v.* ACIDIMETRY.

ALKALI WASTE *v. Soda manufacture*, art. SODIUM.

ALKANET. The Arabic name *Al-henneh*, modified to *alkanna* or *al-kenna*, was originally applied to the lythraceous shrub *Lawsonia alba* (Lam.), the root of which was described as *Radix Alkannæ vera*, in contradistinction to the root of our alkanna, which is *Anchusa tinctoria* (Lam.), and which became known as *Radix Alkannæ spuria tinctoria*. The latter, or *False alkanet*, is also known as *Orcanette*, Fr.; *Orkanet*, Ger.; Languedoc bugloss or Dyers' bugloss, *Radix Alkannæ spuria*. A rough plant with downy spear-shaped leaves, and clusters of purplish or reddish flowers; belongs to the *Boraginaceæ*. Found in Asia Minor, Greece, Hungary, &c. The roots, which have an astringent taste, occur in commerce, varying from the thickness of a quill to that of a finger.

Alkanet is one of the more ancient dyestuffs, having been employed by the Romans, but, on the other hand, it does not appear at any time to have attained such importance as madder, indigo, or even turmeric. The colouring matter of alkanet, known as *anchusin* or *alkannin*, has been examined by several chemists, but it is doubtful whether this compound has as yet been obtained in a chemically pure condition. Its composition is variously given as $C_{17}H_{10}O_4$ (Pelletier, Annalen, 6, 27) $C_{35}H_{20}O_8$ (Bolley and Wydlers, Annalen, 62, 41), $C_{15}H_{14}O_4$ (Carnelutti and Nasini, Ber. 13, 1514), and $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$ (Liebermann and Römer, Ber. 20, 2428).

Alkannin forms a dark-red amorphous powder possessing a beetle-green iridescence, is readily soluble in most of the usual solvents, and its alkaline solution is coloured deep-blue. On distillation with zinc-dust it gives, according to Liebermann and Römer, both methylanthracene and anthracene.

Diacetylalkannin $C_{15}H_{12}O_4(C_2H_3O)_2$ forms a dull yellow micro-crystalline powder (C. and N.).

According to Eriksson (Ber. Deut. pharm. Ges. 1910, 20, 202), alkannin consists of two red pigments, the one being coloured green and the other blue by the action of alkalis. Red crystals have been observed by Tschirch in spaces in the cortex of old specimens of alkanet root. As alkannin is insoluble in water, in dyeing with alkanet an alcoholic extract is usually employed; and with aluminium and iron mordanted fabrics, violet and grey shades are respectively produced. These colours, however, are not fast to light, and are somewhat readily affected by weak alkalis or acids.

Haussmann of Mulhouse introduced alkanet into calico-printing, and for a short time it appears to have played a quite important part, but it is now little if at all employed in Europe for ordinary dyeing purposes. It is still used for colouring artificial wines, pomades, hair-oils, sweets, &c., and for these purposes it is well adapted on account of its ready solubility and harmless nature.

Böttger (J. pr. Chem. 107, 146) and Eng (J. 70, 935) recommend the use of papers stained by alkanet as indicators in alkalimetry.

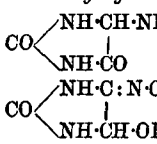
According to Jolin (Chem. Schriften über Alkanna, iv. 84), Thompson (Pharm. J. [3] 16, 860), and Eriksson (*l.c.*), alkanet root contains from 5 to 6 p.c. of anchusin. A. G. P.

ALKANNA or **AL-KENNA.** The powdered roots and leaves of the *Lawsonia alba* (Lam.), used in the East for dyeing the nails, teeth, hair, and garments. Used in Persia mixed with lime for dyeing the tails of horses.

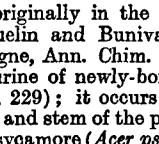
ALKANNIN (ANCHUSIN) *v.* ALKANET.

ALKASAL *v.* SYNTHETIC DRUGS.

ALLANTOIN. *Glyoxyldiureide* $C_4H_6O_3N_4$



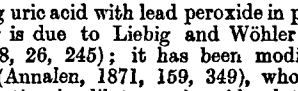
or



was found originally in the allantoic liquid of cows (Vauquelin and Buniva, Ann. Chim. 23, 269; Lassaigne, Ann. Chim. Phys. [2] 17, 301) and in the urine of newly-born calves (Wöhler, Annalen, 70, 229); it occurs also in the young leaves, buds, and stem of the plane tree (*Platanus orientalis*); sycamore (*Acer pseudoplatanus*), and in the bark of the horse-chestnut (*Æsculus hippocastanum*). Under normal conditions of growth 0·25 gram allantoïn may be isolated from 440 grams of fresh young leaves of the plane, but when the branches are cut in bud and the buds allowed to open in water, the amount of allantoïn increases to 0·5 or 1 p.c. of the dried leaves (Schulze and Barbieri, Ber. 1881, 14, 1602; J. pr. Chem. [2] 25, 145; Schulze and Bosshead, Zeitsch. physiol. Chem. 1884, 9, 420). It has been found in the nitrogenous constituents of wheat-germs (Richardson and Crampton, Ber. 1886, 19, 1180); in tobacco seeds (Scurti and Perciabosco, Gazz. chim. ital. 1906, 36, ii. 626); and in crude beet juice (v. Lippman, Ber. 1896, 29, 2652). Allantoïn is a normal constituent of the urine of mammals; the amount varies in different species, being greatest in the dog and least in man (Frericho, Städeler, J. 1854, 7, 714; Wiechowski, Biochem. Zeitsch. 1909, 19, 368; Schittenhelm, Zeitsch. physiol. Chem. 1909, 63, 248, 269, 283, 289). In the case of the dog the amount of allantoïn in the urine is increased after a diet of animal food (Salkowski, Ber. 1878, 11, 500), of calf's thymus (Cohn, Zeitsch. physiol. Chem. 1898, 25, 507; Mendel, Amer. J. Physiol. 6, xiv.–xv.; M'Lachlan, Proc. Roy. Soc. Edin. 1906, 26, 95); it is also increased after the administration of uric acid (Salkowski, Ber. 1876, 9, 719; Swain, Amer. J. Physiol. 1910, 6, 38; Wiechowski, Beitr. Chem. Physiol. Path. 1908, 11, 109; Biochem. Zeitsch. 1910, 25, 431) or of nucleic acid (Mendel, *l.c.*; Schittenhelm, Zeitsch. physiol. Chem. 1910, 66, 53; Wiechowski, *l.c.*). Allantoïn is therefore to be regarded as an end-product of uric acid metabolism in the case of such animals as dogs and rabbits (Wiechowski, *l.c.*; Schittenhelm, *l.c.*).

The method of preparation of allantoïn by

oxidising uric acid with lead peroxide in presence of water is due to Liebig and Wöhler (Annalen, 1838, 26, 245); it has been modified by Mulder (Annalen, 1871, 159, 349), who effects the oxidation in dilute acetic acid solution and in bright daylight; by this method 100 grams of uric acid yield 30–32 grams of allantoïn. A quantitative yield of allantoïn is obtained when uric acid is oxidised by an alkaline solution of potassium permanganate, and the intermediate compound

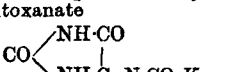


decomposed by acetic acid (Sundvik, Zeitsch. physiol. Chem. 1904, 41, 343; Behrend, Annalen, 1904, 333, 141). Allantoïn is also obtained by the action of nitrous acid on dialuric acid (Gibbs, Annalen Suppl. 1870, 7, 337). The synthesis of allantoïn has been effected (1) by Grimaux (Compt. rend. 1876, 83, 62) by heating a mixture of glyoxylic acid (1 part, and carbamide (2 parts) at 100° for 8–10 hours; (2) by Michael (Amer. Chem. J. 1883, 5, 198) by heating a mixture of mesoxalic acid and carbamide in equal proportions at 110°; (3) and by Simon and Chavanne (Compt. rend. 1906, 143, 51) by the action of ammonia or alkali hydroxides on ethyl allantoate $CH(NH{\cdot}CO.NH_2)_2CO_2Et$, obtained by the condensation of ethyl glyoxylate with carbamide.

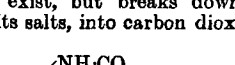
Allantoïn is readily soluble in boiling water, sparingly so in cold (1:131·5 at 21°·8) (Grimaux, Ann. Chim. Phys. 1877, [v] 11, 389); crystallises in glassy monoclinic prisms (Dauber, Annalen, 1849, 71, 511); its heat of combustion at constant pressure is + 413·8 Cal., and heat of formation + 170·4 Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 106).

Allantoïn forms a silver salt $C_4H_5O_3N_4Ag$ (Liebig and Wöhler, *l.c.*) and a potassium salt $C_4H_5O_3N_4K$ (Mulder, *l.c.*); it also combines with certain metallic oxides to form sparingly soluble compounds; the mercury, copper, zinc, lead, and cadmium derivatives are described by Limpricht (Annalen, 1853, 88, 94). (For the method of estimating allantoïn based on the sparing solubility of the silver and mercury derivatives, *see* Loewi, Zeitsch. anal. Chem., 1900, 39, 266; Poduschka, *ibid.* 267.)

Allantoïn is oxidised by potassium ferricyanide in the presence of potassium hydroxide to potassium allantoxanate



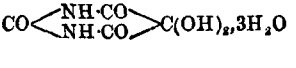
(van Embden, Annalen, 1873, 167, 39); the free acid does not exist, but breaks down, when liberated from its salts, into carbon dioxide and allantoxaïdin



(Ponomareff, Ber. 1878, 11, 2156). M. A. W.

ALLEMONITE. A native alloy of arsenic and antimony, $SbAs_2$, found at Allemont in the Dauphiné, Przibram in Bohemia; and Andreasberg in the Hartz.

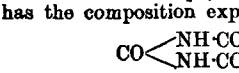
ALLOXAN. Mesoxalylcarbamide



found by Liebig (Annalen, 121, 81) and by Lang (Zeitsch. anal. Chem. 6, 294) in certain pathological excretions, is one of the oxidation products of uric acid, and was first prepared by Brugnatelli (Ann. Chim. Phys. 1817, 8, 201; from Giornale di Fisica, decade seconde i. 117), under the name of *erythric acid*, by oxidising uric acid by means of nitric acid, chlorine or iodine. Liebig and Wöhler (Annalen, 1838, 26, 256), who systematically studied the oxidation of uric acid, gave to this product the name of *alloxan*, regarding it as bearing the same relation to *allantoïn* and *oxalic acid* that *oxaluric acid* does to *oxalic acid* and *urea*. According to Liebig and Wöhler (*l.c.*) and to Gregory (Mem. Chem. Soc. 1848, iii. 44), alloxan can be obtained most readily and with a yield of 90 p.c. by careful oxidation of uric acid by means of nitric acid, sp.gr. 1·412.

According to Schlieper (Annalen, 1845, 55, 261), the oxidation of uric acid to alloxan is more conveniently effected with hydrochloric acid and potassium chlorate; 4 parts of uric acid are mixed with 8 parts of hydrochloric acid, and 1 part of finely powdered potassium chlorate added in successive small quantities, avoiding the liberation of chlorine; after two or three hours the dissolved alloxan is reduced by means of sulphuretted hydrogen to the sparingly soluble *alloxantin*. This is separated from the sulphur by crystallisation from hot water, and oxidised to alloxan by the action of diluted nitric acid.

Alloxan crystallises from warm saturated aqueous solution in large triclinic prisms containing $4H_2O$; on exposure to the air or on heating at 100° it loses $3H_2O$, and the dried compound has the composition expressed by the formula



(Lang, Grailich, J. 1858, 308; Hartley, Chem. Soc. Trans. 1905, 87, 1802); it is also obtained in oblique rhombic prisms, belonging to the monoclinic system on evaporating an aqueous solution at 65°–70°. The remaining molecule of water is lost at 150°.

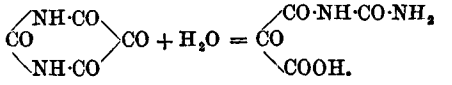
When crystals of alloxan are kept for some years in closed vessels they sometimes undergo spontaneous decomposition, forming alloxantin, parabanic acid, and carbon dioxide. According to Gregory (Annalen, 1853, 87, 126), this is due to the presence of traces of nitric acid contained in the water of crystallisation. Similar phenomena were observed by Baumert (Pogg. Ann. 1860, 110, 93), by Heintz (Pogg. Ann. 1860, 111, 436), and by Otto (Annalen Suppl. 1865, 4, 256). Cases of spontaneous explosive decomposition of alloxan are recorded by Wheeler and by Bogert (J. Amer. Chem. Soc. 1910, 32, 809); the products of decomposition being carbon dioxide, carbamide, oxalic acid, and alloxantin (Gortner, J. Amer. Chem. Soc. 1911, 33, 85).

The molecular heat of combustion of alloxan is 276·5 Cal. (Matignon, Ann. Chem. Phys. 1893, [vi.] 28, 300); the dissociation constant is $2{\cdot}32 \times 10^{-7}$ (Wood, Chem. Soc. Trans. 1906, 89, 1835). In common with the other simple ureides, alloxan shows no absorption bands in its spectrum (Hartley, Chem. Soc. Trans. 1905, 87, 1815).

Alloxan is readily soluble in alcohol or water;

the solution is acid to litmus, stains the skin purple, and imparts to it a curious and unpleasant odour. In its physiological action alloxan affects the central nervous system, producing first stimulation, then paralysis. When taken internally it is excreted in the urine as alloxantin and parabanic acid (Lusini, Chem. Zentr. 1895, ii. 311, 727, 838; Koehne, Chem. Zentr. 1894, ii. 296).

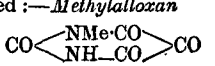
Alloxan is readily oxidised by warm dilute nitric acid, forming carbon dioxide and *parabanic acid* (*oxalylcarbamide*) (*q.v.*); is reduced by sulphuretted hydrogen, stannous chloride, zinc, and hydrochloric acid, or by boiling with excess of sulphurous acid to *alloxantin* (*q.v.*); and is readily hydrolysed by alkali carbonates or by the hydroxides or chlorides of the alkaline earths, forming the corresponding salt of *alloxanic acid*. The barium and calcium salts are insoluble.



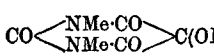
If, however, excess of alkali is employed or the solutions are heated, the hydrolysis is carried to completion with the formation of mesoxalic acid and carbamide (Schlieper, Annalen, 1845, 55, 263; 56, 1). Alloxan gives a deep-blue colour with ferrous salts, but no precipitate is formed unless an alkali is present. According to Agrestini (Boll. Chim. Farm. 1902, 41, 5–7; Chem. Zentr. 1902, i. 631), the formation of blue colour is dependent on the presence of a trace of ammonia or caustic alkali, and the same deep-blue colour is also given by *pure* ferric salts under similar conditions. Alloxan gives the murexide reaction, and Angrestini (*l.c.*) finds that the ammonia in the reaction can be replaced by certain acid amides, amino acids, or substituted amines; Rosenheim's alloxan test for choline (J. Physiol. 1905, 33, 220), namely, the formation of a deep red-violet colour when a drop of a 1 p.c. solution of choline hydrochloride is evaporated on the water-bath with a few drops of a saturated solution of alloxan, is probably a reaction of the same order.

Other tests for alloxan are (1) the formation of a deep violet-blue colour when a solution of alloxan is boiled for a few minutes with a drop of pyrrole. The colour changes to red on cooling, becoming green and then intensely blue on the addition of alkali. (2) The blue-green solution obtained on mixing concentrated sulphuric acid solutions of alloxan (or alloxantin) and pyrocatechol, the colour changes to an intense green on dilution (Agrestini, *l.c.*). Hartley (Chem. Soc. Trans. 1905, 87, 1816) finds that hydrated alloxan, when powdered along with pure calcite, acquires a yellowish-pink tinge. After half an hour the colour is decided and it is permanent; on adding water a red solution is obtained. When alloxan, dried at 100°, is similarly treated, there is no colour developed until water has been added. Alloxanic acid gives no such colour reaction.

The following *homologues* of alloxan have been described:—*Methylalloxan*

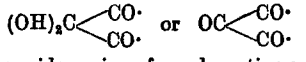


prepared from methyl uric acid (Hill, Ber. 1876, 9, 1092); from ζ-uric acid (Fischer, Ber. 1899, 32, 2731); from theobromine (Maly, Andreasch, Monatsh. 1882, 3, 108; Fischer and Clemm, Ber. 1897, 30, 3090). It crystallises from water in brilliant colourless prisms, becomes anhydrous at 60° in a vacuum, and decomposes at 156°. *Dimethylalloxan*

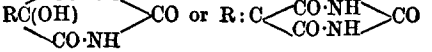


prepared by oxidising caffeine (Fischer, Annalen, 1882, 215, 257; Maly, Andreasch, Monatsh. 1882, 3, 96), by boiling dichlorodimethylbarbituric acid with water or silver oxide (Techow, Ber. 1894, 27, 2083), loses $1H_2O$ when dried over sulphuric acid, decomposes at 100°; the anhydrous compound is a pale yellow powder soluble in alcohol. *Diethylalloxan* $C_8H_{10}O_4N_2$, prepared by oxidising 1 : 3-diethylbarbituric acid with nitric acid, containing a little nitrous acid (Sembritzki, Ber. 1897, 30, 1820). *Methylethylalloxan*, from ethyltheobromine by oxidation (Pommerehne, Apoth. Zeit. 1897, 12, 5). Some derivatives of 1 : 3-diphenylalloxan have been described by Whiteley (Chem. Soc. Trans. 1907, 91, 1344).

Inasmuch as the alloxan molecule contains the mesoxalyl radical



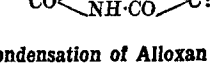
it forms a wide series of condensation products through the medium of the : $C(OH)_2$ or : CO group yielding derivatives of the type



respectively. These compounds will be described under the following eight headings.

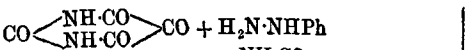
1. **Condensation of Alloxan with Bisulphites.**—Alloxan forms condensation products of the type $C_4H_2N_2O_4,NaHSO_3,1\frac{1}{2}H_2O$ with alkali bisulphites (Limpricht and Wuth, Annalen, 1858, 108, 41), and with the sulphites of certain organic bases (Pellizzari, Annalen, 1888, 248, 146). *Alloxan ethylamine sulphite* $C_2H_7N{\cdot}SO_3H_2{\cdot}C_4H_2N_2O_4,H_2O$; *Alloxan aniline sulphite* $C_6H_7N{\cdot}SO_3H_2,C_4H_2N_2O_4,2H_2O$; *Alloxan methylaniline sulphite* $C_7H_9N{\cdot}SO_3H_2,C_4H_2N_2O_4{\cdot}2H_2O$; *Alloxan dimethylanilinesulphite* $C_8H_{11}N{\cdot}SO_3H_2,C_4H_2N_2O_4,4H_2O$, are described and the crystallographic constants are given. The *benzidine* compound contains $1H_2O$; *toluidine*, *aminobenzoic acid*, and *aspartic acid* yield similar compounds. *Alloxan pyridine sulphite* is triclinic, and anhydrous crystalline derivatives are afforded by *quinoline*, *picoline*, *morphine*, and *cinchonine*; the *strychnine* compound has $1H_2O$, and the *brucine* compound $1\frac{1}{2}H_2O$.

2. **Condensation of Alloxan with Hydroxylamine.**—Alloxan condenses with hydroxylamine hydrochloride (Ceresole, Ber. 1883, 16, 1133) to form the *oxime*, *violuric acid*

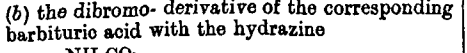


(*q.v.*).

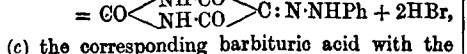
3. **Condensation of Alloxan with Hydrazines.**—Hydrazones of alloxan and its homologues can be prepared by the condensation of (*a*) the alloxan with the hydrazine



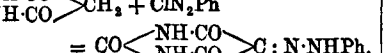
(*b*) the dibromo- derivative of the corresponding barbituric acid with the hydrazine



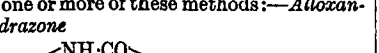
(*c*) the corresponding barbituric acid with the diazonium chloride



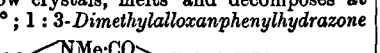
And the following hydrazones have been prepared by one or more of these methods:—*Alloxanphenylhydrazone*



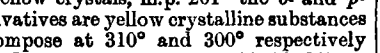
pale-yellow crystals, melts and decomposes at 298°–300°; 1 : 3-*Dimethylalloxanphenylhydrazone*



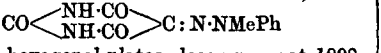
slender yellow crystals, m.p. 261° the *o*- and *p*-nitro derivatives are yellow crystalline substances and decompose at 310° and 300° respectively (Kühling, Ber. 1891, 24, 4140; 1898, 31, 1972); *alloxanphenylmethylhydrazone*



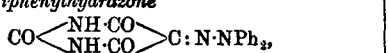
brick-red hexagonal plates, decomposes at 189°–191° (Whiteley, Chem. Soc. Proc. 1906, 22, 201); *alloxandiphenylhydrazone*



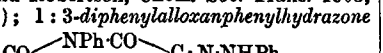
bright-yellow powder, melts above 270° (Armstrong and Robertson, Chem. Soc. Trans. 1905, 87, 1291); 1 : 3-*diphenylalloxanphenylhydrazone*



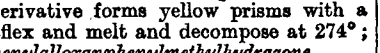
bright-yellow needles that decompose at 265°, the *p-nitro* derivative forms yellow prisms with a purple reflex and melt and decompose at 274°; 1 : 3-*diphenylalloxanphenylmethylhydrazone*



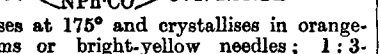
decomposes at 175° and crystallises in orange-red prisms or bright-yellow needles; 1 : 3-*diphenylalloxandiphenylhydrazone*



melts and decomposes at 254°–255°, and forms yellow crystals yielding an orange-red powder on trituration; 1 : 3-*diphenylalloxanphenylbenzylhydrazone*



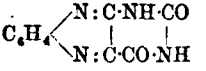
melts and decomposes at 130°, crystallises from benzene in bright-yellow needles, and from methyl alcohol in bright-red prisms; from toluene a mixture of the red prisms and yellow needles is obtained (Whiteley, Chem. Soc. Trans. 1907, 91, 1344); *alloxancyanophenylhydrazone*



from alloxan and aminophenylcyanamide, straw-yellow compound, m.p. 286° (Rolla, Gazz. chim. ital. 1907, 37, i. 623).

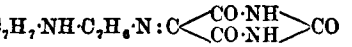
4. Condensation of Alloxan with Semicarbazide.—This reaction has been studied by Bromberg (Ber. 1897, 30, 131). He describes the compounds *alloxansemicarbazide* $C_5H_8O_6N_5$ and *dimethylalloxansemicarbazide* $C_7H_{11}O_5N_5$, but was not successful in determining their constitution.

5. Condensation of Alloxan with Diamines.—In the condensation of alloxan with *o*-diamines the ketonic carbonyl and one of the adjacent carbimido- groups take part, and the product is an *azine*; *alloxazine*

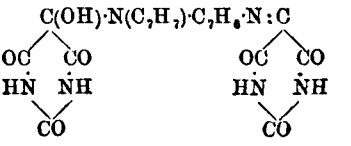


obtained from *o*-phenylenediamine, forms yellow microscopic crystals that decompose above 300°; similar derivatives were obtained from 3 : 4-diaminotoluene and α-β-diaminonaphthalene (Kühling, Ber. 1891, 24, 2363); for the effect of oxidising and reducing agents on these compounds, compare Kühling, Ber. 1895, 28, 1968; 1899, 32, 1650).

The condensation of alloxan with mono-substituted *o*-diamines results in the formation of two compounds according as one or more alloxan molecules take part in the reaction. Thus alloxan condenses with *orthaminoditolylamine* at the ordinary temperature to form *alloxanylorthaminoditolylamine*

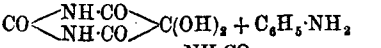


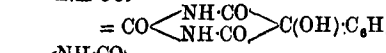
glittering yellow prisms, that melt and decompose at 252°, and dissolve in concentrated sulphuric acid with a deep red colour; if, however, the condensation is effected in the presence of fuming hydrochloric acid and the mixture is boiled, *dialloxanylorthaminoditolylamine*



is formed. It is crystalline, and blackens at 300°, dissolves readily in alkali carbonates, and gives a deep-blue solution in concentrated sulphuric acid. Dimethylalloxan gives similar derivatives (Kühling, Ber. 1893, 26, 540), and similar condensation products are obtained from alloxan and phenyl-*o*-phenylenediamine, *o*-aminodi-*p*-tolylamine, and N-methyl-*o*-phenylenediamine (Kühling and Kaselitz, Ber. 1906; 39, 1314); and from tetramethyl-*m*-phenylenediamine (Sachs and Appenzeller, Ber. 1908, 41, 91).

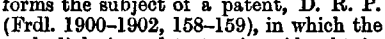
6. Condensation of Alloxan with Aromatic amines.—Alloxan condenses readily with primary aromatic amines (Pellizzari, Gazz. chim. ital. 1895, 17, 419) to form aminoaryl substituted dialuric acids, yielding on hydrolysis with alkali, the corresponding tartronic acid (*q.v.*). Thus aniline and alloxan give *p*-aminophenyldialuric acid, and this on hydrolysis yields *p*-aminophenyltartronic acid





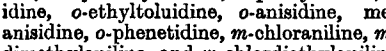
In view of the importance of these compounds as sources of tartronic acids, their preparation forms the subject of a patent, D. R. P. 112174 (Frdl. 1900–1902, 158–159), in which the amino-aryl- dialuric and tartronic acids obtained from the following bases are described: ethylaniline, diethylaniline, benzylaniline, methylbenzylaniline, ethylbenzylaniline, diphenylamine, *o*-toluidine, *o*-ethyltoluidine, *o*-anisidine, methyl-*o*-anisidine, *o*-phenetidine, *m*-chloraniline, *m*-chlordimethylaniline, and *m*-chlordiethylaniline.

By careful oxidation with potassium permanganate of the alkali salts of the tartronic acids, or by oxidising the corresponding dialuric acid with mercuric oxide in presence of potassium hydroxide, the corresponding glyoxylic acid (*q.v.*) can be obtained

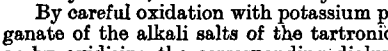


and the preparation by these methods of an important series of glyoxylic acids forms the subject of patents D. R. P. 117021, 26/11, 1900; and 117168, 3/12, 1900.

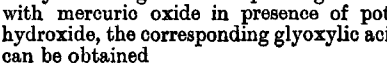
Alloxan condenses also with pyrazolone bases to form derivatives of dialuric acid (tartronylcarbamide), and these on hydrolysis with cold caustic alkali yield the corresponding substituted tartronimides (Pellizzari, Gazz. chim. ital. 1888, 18, 340). Thus *phenylmethylpyrazolonetartronylcarbamide*



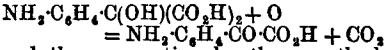
forms long yellow needles that decompose at 170°–178°, and yield *phenylmethylpyrazolonetartronimide*



on hydrolysis; *phenyldimethylpyrazolonetartronylcarbamide*

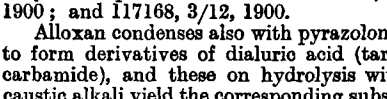


melts and decomposes at 261°, and yields *phenyldimethylpyrazolonetartronimide*



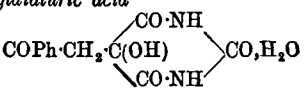
decomposing at 245°–250°.

7. **Condensation of Alloxan with Phenols.**—Alloxan condenses in the presence of hydrogen chloride, sulphuric acid, or zinc chloride with mono- or polyhydroxy- phenols to form derivatives of dialuric acid (tartronylcarbamide), that promise to be of value for pharmaceutical purposes, and are readily converted by hydrolysis into the corresponding tartronic acid:

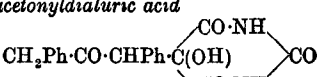


A description of the compounds obtained from alloxan and the phenolic compounds, phenol, *m*-cresol, *p*-cresol, guaiacol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, α-naphthol, is given in D. R. P. 107720, 25/8, 1898; 113722, 9/7, 1900; 114904, 17/9, 1900; and the tartronic acids derived from them are described in D. R. P. 115817, 8/10, 1900.

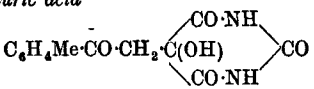
8. **Condensation of Alloxan with Ketones.**—Alloxan condenses with acetophenone and certain of its homologues to form phenacyldialuric acid or its derivatives of which the following are described by Kühling (Ber. 1905, 38, 3003), Kühling and Schneider (Ber. 1909, 42, 1285): *phenacyldialuric acid*



m.p. 212°, with decomposition; the *bromo*-derivative decomposes at 217°; *p-ethoxyphenacyldialuric acid* $C_{14}H_{14}O_6N_2$, m.p. 214°; the *bromo*- derivative, decomposes at 201°; *αγ-diphenylacetonyldialuric acid*



m.p. 233° with decomposition; *p-methylphenacyldialuric acid*



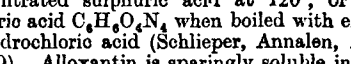
m.p. 241°–242°, with decomposition; the *acetyl* derivative decomposes at 220°, the *benzoyl* at 215°; *p-methoxyphenacyldialuric acid* $C_{13}H_{12}O_6N_2$ decomposes at 227°, and yields an *acetyl* derivative, m.p. 207°. M. A. W.

ALLOXANIC ACID *v.* ALLOXAN.

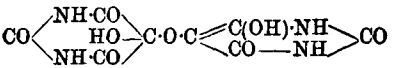
ALLOXANTIN $C_8H_6O_8N_4,2H_2O$ (Ritthausen, Ber. 1896, 29, 892) exists in small quantities in crude beet-juice (Lippmann, Ber. 1896, 29, 2645), and forms 34 to 36 p.c. of the products when *convicin* from sow-beans (*Vicia faba minor*) or from vetches (*Vicia sativa*) is hydrolysed by dilute mineral acids (Ritthausen, *l.c.*; J. pr. Chem. 1899, [ii.] 59, 487). Alloxantin was first prepared by Liebig and Wöhler (Annalen, 1838, 26, 262) by oxidising uric acid with dilute nitric acid; or by the direct union of alloxan and dialuric acid, or by reducing a cold aqueous solution of alloxan with sulphuretted hydrogen or stannous chloride. According to Vitali (Chem. Zentr. 1898, i. 665, from Boll. Chim. Farm. 37, 65), the reduction can also be effected by means of hydriodic acid. Alloxantin was synthesised by Grimaux (Compt. rend. 1878, 87, 752) by heating malonic acid, carbamide and phosphoryl chloride at 150°, and passing sulphuretted hydrogen through a nitric acid solution of the crude product; or by passing sulphuretted hydrogen through a hot aqueous solution of dibromobarbituric acid (Compt. rend. 1879, 88, 86). Koech (Annalen, 1901, 315, 246) describes the conversion of *iso*dialuric acid into alloxantin by heating it with guanidine and acetic acid; the change seems to be due to the transformation of the *iso*dialuric acid into dialuric acid by the action of the base, and the subsequent oxidation of the dialuric acid to alloxantin, since, if the reaction is conducted in an

atmosphere of carbon dioxide, dialuric acid only is obtained.

Alloxantin crystallises from aqueous solutions in small sharp rhombic prisms, containing 2 mols. H_2O; it becomes anhydrous after heating for 1–1½ hours at 150°, or for 5 hours at 107°–110°; it decomposes at 170° into hydurilic acid, ammonia, carbon monoxide, carbon dioxide, and oxalic acid. It is decomposed into barbituric acid and parabanic acid when heated with concentrated sulphuric acid at 120°, or into alliturie acid $C_6H_8O_4N_4$ when boiled with excess of hydrochloric acid (Schlieper, Annalen, 1845, 56, 20). Alloxantin is sparingly soluble in cold water, yielding an acid solution that reduces solutions of silver salts, and gives a characteristic violet-blue precipitate with baryta water, changing on warming into the colourless barium alloxanate which undergoes further decomposition into barium mesoxalate and barium carbonate (Liebig and Wöhler, Annalen, 1838, 26, 312). Alloxantin has a molecular heat of combustion = 584·7 Cals. (Matignon, Ann. Chim. Phys. 1893, [6] 28, 323), and a freshly prepared aqueous solution shows a remarkable absorption band in the ultra-violet, which disappears upon keeping the solution, owing to the decomposition of the alloxantin into alloxan and dialuric acid (Hartley, Chem. Soc. Trans. 1905, 87, 1814). For this reason Hartley expresses the constitution of alloxantin by the formula



(*ibid.* 1819). Piloty and Finckh (Annalen, 1900, 333, 22) found that alloxantin was resolved into alloxan and dimethylamine dialurate, by boiling with dimethylamine acetate, and suggest the constitutional formula



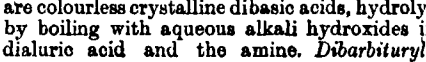
in which the relationship between alloxantin and alloxan is the same as that existing between quinhydrone and quinone.

Alloxantin is readily converted into murexide (*q.v.*) by the action of ammonia, into alloxan by mild oxidising agents, and into dialuric acid by reducing agents. In its physiological action alloxantin resembles alloxan, but is especially poisonous to cold-blooded animals, the blood showing strong reducing properties; when taken internally it appears in the urine as parabanic acid, and in smaller quantities as dialuric acid, murexide, and alloxantin itself (Kowalewski, Chem. Zentr. 1887, 1296; Susini, Ann. Chim. Farm. 1895, 21, 241; 1896, 22, 341, 385).

Acetylalloxantin $C_{10}H_8O_9N_4,H_2O$, obtained by the interaction of acetyl dialuric acid and alloxan, crystallises in thin leaflets, becomes anhydrous when kept in a vacuum over sulphuric acid, melts and decomposes at 263°–265°, and is slowly hydrolysed by hot water with the formation of alloxantin.

Benzoylalloxantin $C_{15}H_{10}O_9N_4,H_2O$, similarly formed from benzoyl dialuric acid and alloxan, crystallises in colourless six-sided plates, and melts at 253°–255° (Behrend and Friedrich, Annalen, 1906, 344, 1).

Alloxantin is decomposed when boiled in an aqueous solution of the hydrochloride of a primary amine, yielding alloxan, together with the corresponding *dibarbiturylalkylamine*. These are colourless crystalline dibasic acids, hydrolysed by boiling with aqueous alkali hydroxides into dialuric acid and the amine. *Dibarbiturylmethylamine*



decomposes at 280°, *dibarbiturylethylamine* decomposes at 235°, *dibarbiturylphenylamine* becomes blue at 240°, *dibarbiturul-α-naphthylamine* becomes black at 260°, the corresponding *β*-compound decomposes at 260°, and *dibarbiturylcarbamide* $CO(NH{\cdot}C_4H_3O_3N_2)_2$ decomposes above 300°.

The following homologues of alloxantin have been prepared: *methylalloxantin* $C_9H_8O_8N_4$, $3H_2O$ from methylalloxan and dialuric acid (Andreasch, Monatsh. 1882, 3, 431); sym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4,4H_2O$ from methylalloxan (Maly, Andreasch, Monatsh. 1882, 3, 109), unsym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4$, H_2O from dimethyldialuric acid and alloxan (Andreasch. Montash. 1882, 3, 428). *Tetramethylalloxantin*, $C_{12}H_{14}O_8N_4$ *amalic* acid (from *ἁμαλός* = *soft*, so called on account of its feebly acid reaction), prepared (1) by oxidising caffeine with chlorine or nitric acid (Rochleder, Annalen, 71, 1); (2) by reducing dimethylalloxan with sulphuretted hydrogen (Fischer, Ber. 1881, 14, 1912) or with stannous chloride (Andreasch, Monatsh. 1895, 16, 19); (3) from dimethyldialuric acid and dimethylalloxan (Maly and Andreasch, Monatsh. 1882, 3, 105); (4) by the electrolysis of caffeine in sulphuric acid solution (Pommerehne. Arch. Pharm. 235, 365). *Tetraethylalloxantin* $C_{16}H_{22}O_8N_4$, obtained by reducing diethylalloxan, melts and decomposes at 162° (Sembritzki, Ber. 1897, 30, 1821). M. A. W.

ALLOXAZINE *v.* ALLOXAN.

ALLOYS *v.* METALLOGRAPHY.

ALLYL. A univalent radicle C_3H_5—, or $CH_2{:}CH{\cdot}CH_2$—, isomeric with *propenyl* $CH_3{\cdot}CH{:}CH<$.

Allyl acetate $CH_3{\cdot}CO_2C_3H_5$, boils at 103°–104°/733·9 mm. (Brühl), and has sp.gr. 0·9376 at 0° (Schiff). It is only slightly soluble in water, and has a rather sharp smell. It is prepared by the action of allyl iodide on silver acetate (Zinin, Annalen, 96, 361; Cahours and Hofmann, Annalen, 102, 295; Brühl, Annalen, 200, 179; Schiff, Annalen, 220, 109).

Allyl acetic acid $C_3H_5{\cdot}CH_2{\cdot}CO_2H$ boils at 187°–189°, and has sp.gr. 0·98416 at 15° (Perkin). It is slightly soluble in water and its smell resembles that of valerianic acid. It is unaffected by reduction with sodium amalgam, but readily unites with two atoms of bromine. It is prepared by hydrolysing allyl acetoacetic acid ethyl ester with dry sodium ethoxide, or by heating allyl malonic acid (Zeidler, Annalen, 187, 39; Conrad and Bischoff, Annalen, 204, 170; Henry, Chem. Zentr. 1898, ii. 663).

The *chloride* $C_3H_5{\cdot}CH_2{\cdot}COCl$ is a thick, pungent-smelling syrup, boiling at 128°/765 mm., and of sp.gr. 1·0739 at 16° (Henry, *l.c.*).

Allylacetone $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_3H_5$ boils at 128°–130°, and has sp.gr. 0·834 at 27°. It is an unpleasant-smelling liquid. It forms an

amorphous compound with sodium bisulphite, and is reduced by sodium amalgam to hexenyl alcohol. It is prepared by hydrolysing allyl acetoacetic acid ethyl ester (70 grams) with crystallized baryta (215 grams) and water (1650 c.c.) (Zeidler, Annalen, 187, 35; Merling, Annalen, 264, 323). Treated with hydroxylamine it yields *allylacetoxime* $CH_3{\cdot}C(:NOH){\cdot}CH_2{\cdot}C_3H_5$, which is a liquid boiling at 188° (corr.), soluble in alcohol, benzene, ether, acids and alkalis.

Allyl alcohol $C_3H_5{\cdot}OH$, *i.e.* $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, occurs in raw wood spirit, but only to the extent of about 0·2 p.c. (Aronheim, Ber. 1874, 1381; Grodzki and Krämer, *ibid.* 1492). It is a pungent liquid with a burning taste, and mixes readily with alcohol, water, or ether. It boils at 96·6° (corr.), and has sp.gr. 0·87063 at 0° and 0·8573 at 15°/15° (Thorpe, Chem. Soc. Trans. 1880, 208).

It is prepared by slowly distilling glycerol (400 pts.) with crystallized oxalic acid (100 pts.) and a little ammonium chloride (1 pt.) to convert any potassium oxalate into chloride. The receiver is changed at 190° and distillation continued up to 260°. The distillate, containing aqueous allyl alcohol, allyl formate, acroleïn, and glycerol, is rectified and dried, first with potassium carbonate, then over solid potash and distilled. When the last traces of water are removed by quicklime it boils at 96°. The yield is one-sixth of the weight of oxalic acid taken (Tollens and Henninger, Bull. Soc. chim. [2] 9, 394; Brühl, Annalen, 200, 174; Linnemann, Ber. 1874, 854). Further purification may be effected by prolonged heating with sodium bisulphite and, after removal of the bisulphite, redistilling several *times* from quicklime (Thorpe).

It is oxidised by chromic acid solution to acroleïn and formic acid; and by dilute nitric acid to formic and oxalic acids; whilst potassium permanganate produces acroleïn, glycerol, and formic acid. It combines directly with chlorine bromine, iodine chloride, and cyanogen, producing additive products. It is partially reduced by boiling for some hours with zinc and dilute sulphuric acid to *n*-propyl alcohol. Potassium displaces the hydroxylic hydrogen atom and forms gelatinous potassium allylate.

Denigès (Bull. Soc. chim. 1909, 5, 878) describes the following colour reactions for the detection of allyl alcohol, depending on the formation of (1) glyceraldehyde and (2) dihydroxyacetone and the condensation of these products with various reagents. Bromine water (0·6 c.c. in 100 c.c. water) is added to 0·1 c.c. of allyl alcohol, till a slight permanent colouration is produced, and the liquid is then boiled, cooled, and divided into portions of 0·4 c.c. To each of these 0·1 c.c. of a 5 p.c. solution of codeine, resorcinol, thymol, or β-naphthol is added, followed by 2 c.c. of sulphuric acid (sp.gr. 1·84) and the mixture warmed during 3 or 4 minutes at 100°. Codeine and thymol give reddish-violet colourations, resorcinol wine-red, and β-naphthol yellow with greenish fluorescence. The second series of colour reactions is obtained by adding to the brominated liquid above described 5 c.c. of bromine water (0·6 c.c. in 100 c.c. water), heating during 20 minutes at 100°, then boiling to remove excess of bromine and cooling. This liquid contains dihydroxyacetone, and in the presence of concentrated sulphuric acid gives a deep-blue colour with codeine, orange-red with resorcinol, blood-red with thymol, or green with green fluorescence with β-naphthol (Denigès, Compt. rend. 148, 172 and 282).

Allylamines.

Monoallylamine $C_3H_5{\cdot}NH_2$ is a liquid boiling at 53·3° and of sp.gr. 0·7799 at 4° and 0·7688 at 15° (Perkin, Chem. Soc. Trans. 1889, 697); b.p. 58° and sp.gr. 0·864 at 15° (Rinne, Annalen, 168, 262); b.p. 56°–56·5°/756·2 mm. (Schiff, Ber. 1886, 565). It is prepared from allyl *iso*cyanate and potash, or from allyl iodide and ammonia, or by reduction of allyl mustard oil with zinc and hydrochloric acid (Oeser, Annalen, 134, 8). It possesses a penetrating smell, which excites tears and produces sneezing. It is miscible with water in all proportions, and is a strong base, forming a crystalline platinichloride $(C_3H_5{\cdot}NH_2)_2PtCl_6$, and sulphate $(C_3H_5{\cdot}NH_2)_2H_2SO_4$. The hydrochloride melts at 105°–110° (Delépine, Bull. Soc. chim. [3] 17, 294) and the picrate at 140°–141° after sintering (Gabriel and Eschenbach, Ber. 1897, 1125).

Diallylamine $(C_3H_5)_2NH$ boils at 111° and is prepared from allylamine and allyl bromide (Ladenburg, Ber. 1881, 1879; Liebermann and Hagen, Ber. 1883, 1641).

Triallylamine $(C_3H_5)_3N$ is a very unpleasant-smelling liquid, boiling at 150°–151° (Pinner, Ber. 1879, 2054); 155°–156°, sp.gr. 0·8094 at 14·3° (Zander, Annalen, 214, 151). It is prepared by distilling tetrallylammonium bromide with large excess of recently fused potash (Grosheintz, Bull. Soc. chim. [2] 31, 391) or from allyl chloride and alcoholic potassium cyanide in the cold (Pinner, *l.c.*); or from allyl chloride and ammonia (Malbot, Bull. Soc. chim. [2] 50, 90). It is displaced from its aqueous solution by potash, and forms a crystalline platinichloride and hydrochloride.

Tetrallylammonium bromide $(C_3H_5)_4NBr$ is a crystalline solid, soluble in alcohol and water, but only slightly so in ether. It is prepared by leading a stream of ammonia into an alcoholic solution of allyl bromide. The product is purified by recrystallisation from alcohol containing a little ether (Grosheintz, Bull. Soc. chim. [2] 31, 390). Treated with moist silver oxide it yields tetrallylammonium hydroxide.

Tetrallylammonium iodide $(C_3H_5)_4NI$ is the main product of the reaction of allyl iodide on ammonia at the ordinary temperature (Cahours and Hofmann, Annalen, 102, 305; Malbot, Ann. Chim. Phys. [6] 13, 488). It is a crystalline solid, insoluble in strong potash solution.

Allylaniline $C_6H_5{\cdot}NHC_3H_5$ is a yellow oil produced by the action of allyl iodide on aniline. It boils at 208°–209° and has sp.gr. 0·982 at 25° (Schiff, Annalen Suppl. 3, 364).

Diallylaniline $C_6H_5{\cdot}N(C_3H_5)_2$ is prepared by adding allyl bromide (1 mol.) to aniline (1 mol.) in a flask fitted with reflux condenser, separating the allyl aniline by the addition of potash, and converting it into diallyl aniline by repeating the process with more allyl bromide (1 mol.). It boils at 243·5°–245°, and has sp.gr. 0·9538 at 19·8° (Zander, Annalen, 214, 149).

Allyl benzene $C_6H_5{\cdot}CH_2{\cdot}CH{:}CH_2$ is obtained by heating together benzene, allyl iodide and

zinc-dust to 100° (Chojnacki, *J.* 1873, 559; Fittig, Annalen, 172, 132). It boils at 155°. The isomeric *propenyl benzene* (and phenyl propylene—$C_6H_5 \cdot CH:CH \cdot CH_3$) is sometimes incorrectly referred to as allyl benzene.

Allyl bromide, *monobrompropylene* $CH_2:CH.CH_2Br$, boils at 70°–71°, and has sp.gr. 1·4336 at 17° (Zander, Annalen, 214, 144). It is formed by the action of phosphorus tribromide on allyl alcohol, and is prepared by dropping allyl alcohol into a hot solution of potassium bromide in sulphuric acid (1 vol. acid to 1 vol. H_2O) according to Grosheintz (Bull. Soc. chim. [2] 30, 78); or by saturating allyl alcohol with hydrogen bromide at 0° and subsequently heating to boiling for several hours (Jacobi and Merling, Annalen, 278, 11).

Allyl chloride $CH_2:CH \cdot CH_2Cl$ boils at 46°, and has sp.gr. 0·9547 at 0° (Tollens, Annalen, 156, 154); 0·9371 at 19·3° (Zander, Annalen, 214, 142). It is prepared by the action of mercuric chloride on allyl iodide, or from allyl oxalate calcium chloride and alcohol at 100° (Oppenheim, Annalen, 140, 205); or, best, by heating allyl alcohol and concentrated hydrochloric acid to 100° for some hours (Eltekow). It combines with hydrogen chloride to form *propylene chloride* $C_3H_6Cl_2$, and with fuming hydrobromic acid yielding 1-chloro-3-bromopropane $CH_2Cl \cdot CH_2 \cdot CH_2Br$.

Allyl cyanamide, *sinamine*, $C_3H_5 \cdot NH \cdot CN$, is produced by warming allyl thiocarbamide with lead hydroxide on the water-bath (Will, Annalen, 52, 15). On standing for some months crystals separate from the resulting product. It is prepared by shaking an aqueous solution of allyl thiocarbamide with mercuric oxide until the solution no longer blackens ammoniacal silver nitrate (Andreasch, Monatsh. 2, 780). It is alkaline in reaction, precipitating metallic oxides and replacing ammonia in its salts. The crystals contain $\frac{1}{2}H_2O$ and melt at 100°, giving up their water. It forms a difficultly crystallisable salt with oxalic acid, but not with other acids, and double compounds with mercuric and platinic chlorides.

Allyl cyanide, *crotononitrile*, $C_3H_5 \cdot CN$, boils at 119° (corr.), and has sp.gr. 0·8491 at 0° and 0·8351 at 15°. It is obtained by the action of allyl iodide on potassium cyanide, and, together with other products, by allowing allyl mustard oil to remain in contact with water for some weeks, and also by the action of acetic anhydride on crotonaldoxime. It has been prepared by Henry (Chem. Zentr. 1898, ii, 662) by the action of phosphorus pentoxide on α- or β-hydroxy-butyronitrile. It is a liquid with an unpleasant, onion-like smell. On warming to 50°–60° with fuming hydrochloric acid for two hours, chlorobutyric acid is produced. Chromic acid oxidises it to acetic acid, nitric acid to oxalic acid.

Allylenes. Two allylenes are possible and known: symmetrical allylene $CH_2:C:CH_2$, and unsymmetrical allylene $CH_3 \cdot C:CH$.

Symmetrical allylene, *propadiene*, $CH_2:C:CH_2$, is a gas which burns with a sooty luminous flame. It is prepared by dropping α-bromoallyl bromide (10 grams) into a mixture of 20 grams zinc-dust and 25 grams alcohol (70 p.c.) (Gustavson and Demjanow, J. pr. Chem. [2] 38, 202). It does not precipitate ammoniacal solutions of silver nitrate or cuprous chloride. It is readily absorbed by strong sulphuric acid, and acetone is produced on dilution. When dissolved in absolute ether and heated with sodium to 100°, it changes into the isomeric methyl acetylene. It readily forms a tetrabromide $C_3H_4Br_4$ by addition of bromine.

Unsymmetrical allylene, *methyl acetylene* $CH_3 \cdot C\,CH$, results from propylene bromide, monobromopropylene, or monochloropropylene by withdrawal of HCl or HBr by means of alcoholic potash, and from symmetrical allylene (*v. supra*). It is an unpleasant-smelling gas, which is liquefied under a pressure of 3–4 atmospheres. It burns with a bright sooty flame. It dissolves readily in ether (30 vols. in 1 of ether at 16°). Potassium permanganate in the cold oxidises it to formic, oxalic, and malonic acids. Explosive compounds are produced by leading it into ammoniacal solutions of silver nitrate or cuprous chloride. Concentrated sulphuric acid readily absorbs it, forming on dilution and distillation acetone mesitylene and allylene sulphonic acid $C_3H_3SO_3H$ (Schrohe, Ber. 1875, 18 and 367). The *barium salt* of the latter is crystalline, easily soluble, and not decomposed on boiling with water.

Allyl ether $C_3H_5 \cdot O \cdot C_3H_5$ boils at 94·3° and has sp.gr. 0·8046 at 18°. It is prepared from allyl iodide and sodium allyl alcoholate, or from allyl iodide and mercuric oxide (Cahours and Hofmann, Annalen, 102, 290; Berthelot and Luca, Ann. Chim. Phys. [3] 48, 291).

Allyl ethyl ether $C_3H_5 \cdot O \cdot C_2H_5$ boils at 66°–67°/742·9 mm. (Brühl, Annalen, 200, 178). Prepared from allyl iodide and sodium ethoxide.

Allyl iodide C_3H_5I boils at 102·5°–102·8° and has sp.gr. 1·8293 at 23°. Berthelot and Luca, Ann. Chim. Phys. [3] 43, 257) obtained it by the action of PI_3 on glycerol. It may be prepared by leaving together for 24 hours red phosphorus (20 grams), allyl alcohol (160 grams), and iodine (254 grams) (Tollens and Henninger, Annalen, 156, 156); or by the following process: 100 grams of iodine and 1500 grams of carefully dehydrated glycerol are brought together in a large vessel, the air displaced by a current of carbon dioxide, and 300 grams of ordinary phosphorus gradually added. The allyl iodide is distilled off in a stream of carbon dioxide, and then contains as impurity some *iso*propyl iodide. To purify it from this it is dissolved in alcohol and shaken with mercury, when the compound HgC_3H_5I is precipitated. This is recrystallised from water and decomposed, regenerating allyl iodide, by distillation with water and the theoretical quantity of iodine (Linnemann, Annalen Suppl. 3, 263). It combines with bromine to form tribromhydrin, and with hydriodic acid to give diiodopropylene. By long heating with about 20 parts of water it is converted into allyl alcohol and hydriodic acid.

Allyl mercaptan C_3H_5SH boils at 90°. With mercuric chloride it yields C_3H_5SHgCl, which crystallises from alcohol in plates (Hofmann and Cahours, Annalen, 102, 292; Gerlich, Annalen, 178, 88).

Allylmethylal *isothiocyanate* is the name given to the compound $C_3H_5O \cdot S \cdot CH_2 \cdot CN$, prepared by passing a current of formaldehyde gas through glycerol (1 kilo) and allyl *iso*thiocyanate (5 grams) heated to 190° until the weight of the whole is 1400 grams. When cool the product

is filtered and the resulting methylal *iso*thiocyanate used as an antiseptic (Piot, Fr. Pat. 330988, 1903).

Allyl mustard oil *v.* MUSTARD OIL and ESSENTIAL OILS.

Allyl nitrite $C_3H_5NO_2$ is obtained by adding glycerol trinitrite to ice-cold allyl alcohol and cautiously distilling off the allyl ester (Bertoni, Gazz. chim. ital. 15, 364). It boils at 43·5°–44·5°, and has sp.gr. 0·9546 at 0°. It is readily decomposed by shaking with water, and yields ethyl nitrite on treatment with ethyl alcohol.

Allyl-phenyl-thiourea $SC\langle^{NH\cdot C_3H_5}_{NH\cdot C_6H_5}$ may be prepared from aniline and mustard oil (Zinin, Annalen, 84, 348); or from allylamine and phenyl mustard oil (Weith, Ber. 8, 1529). It forms monoclinic crystals, melting at 98°, and is readily soluble in ether, but not in water.

Allyl pyrrol $C_4H_4NC_3H_5$ is readily obtained by the action of allyl bromide on potassium pyrrol in ether (Ciamician and Dennstedt, Ber. 1882, 2581). It is a light-yellow oil, turning brown on exposure to air. It boils at 105°/48 mm. It is insoluble in water, but dissolves in HCl, producing a red colour.

Allyl sulphate $C_3H_5\cdot HSO_4$ is prepared by adding allyl alcohol (1 vol.) to sulphuric acid diluted with its own volume of water (1 vol.), and leaving at ordinary temperatures for five days. Subsequently the mixture is heated to 70° for 12 hours, diluted with water (10 vols.), and saturated with barium carbonate (Szymanski, Annalen, 230, 44; *v.* also Cahours and Hofmann, Annalen, 102, 293). It forms characteristic salts, a number of which are described by Szymanski (*l.c.*).

Allyl sulphide, *oil of garlic*, (Ger. *Knoblauchöl*) $(C_3H_5)_2S$, occurs in garlic (*Allium sativum*) and other plants. It is prepared from mustard oil and potassium sulphide at 100° (Wertheim, Annalen, 55, 297); or from allyl iodide and potassium sulphide (Hofmann and Cahours, Annalen, 102, 291). It is a liquid boiling at 138·6°, and has sp.gr. 0·88765 at 26·8°/4°. It has a very strong odour of garlic and is only slightly soluble in water.

Allyl thiocarbamide, *allyl thiourea, thiosinamine*, '*Rhodallin*' $SC\langle^{NH_2}_{NH\cdot C_3H_5}$, is produced by the prolonged action of aqueous ammonia on mustard oil (Dumas and Pelouze, Annalen, 10, 326). It forms clear six-sided tables, which melt at 78·4°, after sintering at 71°. It is insoluble in benzene, sparingly soluble in water, and readily so in alcohol and ether. It combines directly with halogens, cyanogen, ethyl iodide, acids, &c. Deprived of its sulphur by mercuric oxide, or lead oxide, it yields *sinamine* (allyl cyanamide) $C_3H_5\cdot NH\cdot CN$. It has been used in surgery for the removal of scar tissue, being injected as a 10 or 15 p.c. solution in dilute glycerol.

Allyl tribromide, '*Tribromhydrin*' $C_3H_5Br_3$, was obtained by Wurtz by treating allyl iodide with bromine, and by Berthelot and Luca by the action of phosphorus tri- and pentabromides on glycerol. It is a slightly yellow liquid of sp.gr. 2·430 at 15·5°, and boils at 217°. It is a strong sedative and anodyne.

Allyl urea $OC\langle^{NH_2}_{NH\cdot C_3H_5}$ crystallizes in needles, melting at 85° (Cahours and Hofmann, Annalen, 102, 299; Andreasch, Monatsh. 5, 36).

J. A. P.

ALMASCA. A soft grey resin soluble in chloroform, ether, and absolute alcohol. Probably derived from the burseraceous *Protium heptaphyllum* (March.) [*Icica heptaphylla* (Aubl.)] (Symes, Pharm. J. [3] 13, 213).

ALMATEIN. Trade name for a condensation product of hæmatoxylin and formaldehyde. Used as an antiseptic.

ALMIRAO. Indian name for *Launœa pinnatifida* (Cass.) *Microrhynchus sarmentosus* (DC) which belongs to the family Compositæ and is used at Goa as a substitute for taraxacum (Dymock, Pharm. J. [3] 6, 730).

ALMOND. The kernel of the fruit of *Prunus amygdalus* or *Amygdalus communis*.

Two principal varieties exist—the sweet and the bitter almond. Both contain amygdalin, but the latter is much richer in this substance (2 to 3 p.c.), and contains an enzyme, *emulsin*, which, in the presence of water, decomposes the amygdalin, yielding glucose, benzaldehyde, and hydrocyanic acid

$$C_{20}H_{27}NO_{11}+2H_2O = C_6H_5CHO+HCN+2C_6H_{12}O_6.$$

In addition, almonds contain about 50 p.c. of their weight of a fixed oil (mainly oleïn, and liable to become rancid) and smaller quantities of proteïns, sugar, starch, gum, fibre, and ash.

Analyses of almonds made at various stages of growth and ripening, show the percentage of amyloses, glucose, and saccharose to steadily diminish, whilst the proportion of oil increases (Du Sablon, Compt. rend. 1896, 123, 1084).

According to Vallée (Compt. rend. 1903, 136, [2] 114), reducing sugars in the immature almond decrease as the fatty oil increases; sucrose increases until oil-formation begins, then decreases during oil-production, and towards the end again increases. Ripe almonds contain about 3 p.c. of sucrose. According to Osborne and Campbell (J. Amer. Chem. Soc. 1896, 18, 609), the proteïn in almonds is *amandin* and not conglutin or vitellin.

H. I.

ALMOND OIL is obtained from the seeds of *Prunus amygdalus* (Stokes) [*Amygdalus communis*, (Linn.)]. The almond tree appears to have been indigenous to Turkestan and Middle Asia, and has been transplanted from there to Greece, Italy, Spain, France, and to Northern Africa. The mean percentage composition of the almond is given by König as follows:—

Oil	41·00 p.c.
Water	27·72 „
Albuminoids	16·50 „
Extracted matter, free from nitrogen	10·2 „
Crude fibre	2·81 „
Ash	1·77 „
	100·00

The commercial oil is chiefly expressed from bitter almonds, the seeds of *Prunus amygdalus*, var. *amara*. Bitter almonds contain, besides the oil, amygdalin and emulsin, which give rise to the formation of benzaldehyde, glucose, and hydrocyanic acid. Hence the press-cakes

from almonds find a profitable outlet in the manufacture of genuine 'ethereal bitter almond oil,' by triturating the meal with water.

Sweet almonds (from *Prunus amygdalus*, var. *dulcis*) are but rarely used alone for the preparation of almond oil. Mogador bitter almonds, which are chiefly used in this country for the manufacture of almond oil, are always more or less mixed with sweet almonds. Sweet almonds yield from 44–55 p.c. of oil, bitter almonds yield less and may contain as low a proportion of oil as 20 p.c. On an average, however, bitter almonds yield from 38 to 45 p.c. of oil.

The oil is pale yellow; it has a very pleasant, mild taste, and is almost free from odour. The specific gravity of the oil varies from 0·917 to 0·9195 at 15°. The oil solidifies at −15°, has the saponification value of the majority of oils which are free from volatile acids, and an iodine value of 93–100. This points to the presence of linolic acid, of which about 10 p.c. may be contained, on an average, in almond oil, the remainder being practically oleic acid, since the oil contains no stearic acid, and is most likely also free from palmitic acid.

Almond oil is chiefly used in pharmaceutical practice. Owing to its high price almond oil is largely adulterated with other oils of the *Prunus* family, chiefly with apricot kernel oil, from *Prunus armeniaca* (Linn.), and with peach kernel oil, from *Prunus persica* (Sieb. et Zucc.). These two oils are very similar to almond oil; they differ from it by their higher iodine values, and in having a less pleasant taste than almond oil. They are used to such an extent as adulterants that frequently they completely substitute almond oil; indeed 'foreign' almond oil, or 'oil of sweet almonds, French' (*Oleum amygdalarum gallicum*), is nothing else than a mixture of apricot kernel oil and peach kernel oil. Genuine almond oil is sold in commerce under the name 'almond oil, English.'

The close relationship in which apricot and peach kernel oils stand to almond oil, renders their detection in almond oil a difficult problem. For methods of solving it the reader is referred to Lewkowitsch, Chemical Technology and Analysis of Oils, &c. ii. 234. J. L.

ALMONDS, BITTER, *Essential oil of* (*v.* BENZALDEHYDE; also OILS, ESSENTIAL).

ALOË. A genus of succulent plants, having stiff, pointed, fleshy leaves, belonging to the Liliaceæ. (Plants figured, and structure of leaves described, Pennetier, 560, 579.) Of the 85 species 60 are natives of Cape Colony, and the other species are mainly sub-tropical African, though a few occur in the tropics; a number of species have been, however, introduced into the West and East Indies. (For a list of the species and their distribution, *v.* Pharm. J. [3] 11, 746.)

The fibre is used for rope, &c.; experiments made in Paris have shown it to be five times as strong as hemp. The fibre has also been used for paper-making (Nat. 20, 484).

ALOË RESINS *v.* ALOES OR BITTER ALOES.

ALOES or BITTER ALOES. (*Aloès*, Fr.; *Aloë*, Ger.) The inspissated juice or extract of the aloe. The principal varieties found in the market are:—

1. *Barbados Aloes* (aloes in gourds. The juice of *A. vera* (Linn.) growing in Barbados, Jamaica, and St. Helena. It is opaque, lustreless, and of a brown colour, with a bitter nauseous taste and very disagreeable odour; it gives a powder of a dull-yellow colour.

2. *Cape Aloes* (*A. Perryi*, *A. lucida*?), obtained from *A. spicata*, *A. africana*, *A. ferox*, and other Cape species. Its odour is stronger and more disagreeable than that of Barbados aloes; it is of a deep greenish-brown colour, is resinous and shining, and its powder is of a greenish-yellow colour, and is almost completely soluble in boiling water.

3. *Hepatic Aloes.* Imported from Bombay and Madras. It is probably the juice of the Socotrine aloe solidified without the aid of artificial heat (Pereira, Pharm. J. [3] 11); it is of an opaque liver colour, its powder contains much matter insoluble in weak alcohol.

4. *Socotrine Aloes.* The juice of *A. Perryi* (Baker) imported from Bombay and Madras. It is of a garnet-red to golden-red colour, is aromatic, and has an intensely bitter taste; its powder is of a bright golden-yellow colour (Cooley, 1).

5. *Zanzibar Aloes*, from Zanzibar.

Aloïns. By extracting aloes with water the purgative principles, aloïns, can be obtained. Shenstone (Pharm. J. [3] 13, 461; Chem. Soc. Trans. 44, 480) divides them into two classes: 1. *Nataloïns*, which only yield picric and oxalic acids with nitric acid, and which are not reddened by it, even on heating (Flückiger, Arch. Pharm. [2] 149, 11; Tilden, Chem. Soc. Trans. 25, 153). 2. *Barbaloïns*, which yield aloetic acid $C_{14}H_4(NO_2)_4O_2$, chrysammic acid $C_{14}H_2(NO_2)_4(OH)_2O_2$, picric and oxalic acids, and are reddened by nitric acid. *α-Barbaloïns*, from Barbados aloes reddened in the cold by strong nitric acid (Tilden, Pharm. J. [3] 2, 845; Chem. Soc. Trans. 25, 488). *β-Barbaloïns*, from Socotrine, Zanzibar, and Jafferabad aloes, coloured only on heating with ordinary, and in the cold with fuming, nitric acid (Flückiger, *l.c.*; Tilden, Chem. Soc. Trans. 28, 1270; Pharm. J. [3] 4, 208).

Barbados aloes, analysed by Tschirch and Pedersen (Arch. Pharm. 236, 200), was found to contain 12·25 p.c. *barbaloïn*, 12·65 p.c. resin, 1·75 p.c. ash, 10·5 p.c. amorphous constituents soluble in water, and 0·15 p.c. of an orange colouring matter, *aloe-emodin* $C_{16}H_{10}O_5$, m.p. 216°. Barbaloïn $C_{16}H_{18}O_7$ or $C_{16}H_{16}O_7$(?) was isolated by Smith (Chem. Gaz. 1851, 107), and first examined by Stenhouse. It consists of pale-yellow needles, which melt at 147° and readily become discoloured when moist. Leger (Compt. rend. 125, 185; 127, 234), by recrystallisation of partially purified barbaloïn from methyl alcohol, has obtained *isobarbaloïn*, isomeric with barbaloïn. *Iso*barbaloïn crystallises from methyl alcohol in efflorescent crystals with three mols. of methyl alcohol, or from water with two mols. of water of crystallisation. On fusion with caustic potash, barbaloïn yields orcin, *p*-hydroxybenzoic and aloretic acids (Hlasiwetz, Annalen, 134, 237; 136, 31), and on oxidation with chromic acid breaks up into carbon dioxide, acetic acid, and *aloexanthin* (Tilden, Pharm. J. [3] 8, 231; Chem. Soc. Trans. 32, 264, 903). Oesterle and Babel (Chem. Zentr. 1904, ii. 340) have shown, however, that Tilden's aloexanthin is a mixture of aloe-emodin and rhein, the latter compound

being identical with the rhein isolated from rhubarb by Hesse (Annalen, 309, 43).

The resin from Barbados aloes on hydrolysis gives cinnamic acid and a resin alcohol *aloresinotannol* $C_{22}H_{26}O_8$, consisting of a greyish-brown powder (Tschirch and Pedersen). By the action of alcoholic hydrogen chloride, Oesterle (Arch. Pharm. 237, 81) obtained a trihydroxymethylanthraquinone $C_{15}H_{10}O_5$, m.p. 224°, identical with the aloe-emodin of Tschirch and Pedersen; also Leger (Compt. rend. 134, 1111) has obtained aloe-emodin by treatment of barbaloïn or *iso*barbaloïn with sodium peroxide.

According to Leger (J. Pharm. Chim. iv. 20, 145; Compt. rend. 150, 983), both barbaloïn and *iso*barbaloïn left in contact with alcohol for a long time, give a pentose aloïnose. This sugar has since been shown by Leger (Compt. rend. 150, 1695) to be identical with *d-arabinose*.

The aloïn from Natal aloes has the composition $C_{24}H_{26}O_{10}$, with varying amounts of combined water. It softens at 180° and melts with decomposition at 210°. On acetylation a penta-acetyl derivative is formed. *Nataloïn* differs from barbaloïn by its resistance to alkalis, and by containing a methoxyl group (Groenwold, Arch. Pharm. [3] 28, 115). Leger (Compt. rend. 128, 1401) has isolated two aloins from Natal aloes: *nataloïn*, the compound more soluble in methyl alcohol, to which he gives the formula $C_{16}H_{18}O_7$; and *homonataloïn* $C_{15}H_{16}O_7$, the less soluble constituent. Tschirch and Klaveness (Arch. Pharm. 239, 231), however, could not detect any substance corresponding with Leger's homonataloïn.

The resin from Natal aloes when hydrolysed gives *nataloresinotannol* $C_{22}H_{18}O_4(OH)_4$, consisting of a brown powder, and *p*-coumaric acid. Nataloresinotannol gives a tetra-benzoyl derivative; it yields oxalic and picric acids when oxidised with nitric acid, and on fusion with potash gives phloroglucinol and fatty acids.

Nataloïn, heated with sodium peroxide, yields nataloemodinmethylether, m.p. 238°, which on heating with concentrated hydrochloric acid is converted into nataloemodin, consisting of orange-red needles, melting at 220·5° (Leger).

The aloïns from Curaçao, Cape Socotra, Uganda, and Jafferabad aloes are probably identical with barbaloïn. *Zanaloïn* from Zanzibar aloes appears to be different (Leger, J. Pharm. 25, [vi.] 513; Tschirch and Hoffbauer, Arch. Pharm. 243, 399). The latter chemists show that Barbados aloes contain but little *iso*aloïn, Jafferabad none, whilst that from Curaçao contains a considerable proportion.

Uses.—Chiefly in medicine and as a hop-substitute. It has also been used as a source of certain dyeing materials (Ure, 1, 104; Preston, Chem. Zentr. 1876, 390; Chem. Soc. Trans. 32, 378). Kayser (Chem. Tech. Report, 1876–80) finds aloe colouring matters make certain aniline dyes faster.

Properties and Reactions.—Pure aloes is soluble in ether and almost completely soluble in water, the solution being coloured dark-brown by alkalis, black by ferric chloride, and grey by lead acetate (Flückiger). By adding a solution of copper sulphate or chloride to a solution of aloes, an intense yellow-coloured solution is obtained, which, warmed with potassium bromide or chloride, turns to a deep-red and reddish-violet tint (Klunge, Ber. 16, 691; Arch. Pharm. 1883, 363). This reaction is due to *iso*barbaloïn, for barbaloïn, recrystallised several times from methyl alcohol, does not give the test (Leger, Compt. rend. 131, 55). Borntträger (Zeitsch. anal. Chem. 19, 165; Ber. 13, 1040) extracts with twice the volume of benzene, and adds to the clear extract a drop of ammonia, when, on warming and shaking, the solution becomes violet-red; Groves (Pharm. J. [3] 11, 1045) finds that this colour is not due to aloïn, but probably to a tannin-like substance. According to Tschirch and Pedersen, this test depends on the presence of aloe-emodin. Lenz (Zeitsch. anal. Chem. 21, 220) extracts with amyl alcohol, evaporates the extract, treats with nitric acid, and then with potassium cyanide and hydroxide, when a blood-red colouration is obtained. Cripps and Dymond (Pharm. J. [3] 15, 633) test for aloïn by dissolving 1 grain in 16 drops of strong sulphuric acid, then adding 4 drops of nitric acid (1·42) and 1 ounce of water, when a deep orange or crimson colour is produced, deepened by ammonia; substances containing chrysophanic acid behave in a similar manner, but their aqueous solution turns pink upon the addition of ammonia. Aschan (Arch. Pharm. 241, 340) gives in tabular form a comparison of the reactions of the chief varieties of aloes.

For the estimation of aloïn in aloes, Schaefer (Jour. Pharm. [vi.] 5, 296) recommends the following: 50 grams of aloes are dissolved in 300 c.c. of warm water to which a few drops of hydrochloric acid have been added. When cold the solution is separated from the resin, 50 c.c. of 20 p.c. aqueous ammonia and a solution of 15 grams of calcium chloride in 30 c.c. of water are added, and the whole rapidly shaken. At the end of fifteen minutes the precipitate is separated and triturated in a mortar with hydrochloric acid. The free aloïn and the calcium chloride are dissolved in as little water as possible, filtered if necessary, and the residue washed with boiling water. The aloïn separates from the aqueous solution on cooling. A. S.

ALOES, ESSENTIAL OIL OF. A pale-yellow mobile liquid to which the odour of aloes is due. Sp.gr. 0·863, boils at 266°–271°. It exists in small quantities in aloes, and when pure has the taste and odour of peppermint (Pharm. J. [3] 10, 613).

ALOES WOOD. A name applied to the wood of *Aquillaria Agallocha* (Roxb.), a leguminous tree of Cochin China, and to that of *A. malaccensis* (Lam.) of tropical Asia. Both are highly fragrant and aromatic; used in fumigations and pastilles, and occasionally by cabinet-makers and inlayers.

The same name is applied to the resin. Of all perfumes this is said to be the most esteemed by Orientals.

ALOIN *v.* GLUCOSIDES.

ALOO BOKHARA, ALPOGADA, PAZHAM. The Bokhara plum (*Prunus insititia* (Linn.) [*P. bokhariensis*], largely imported into Bombay. Used as a laxative. The root is astringent; the gum is used as a substitute for gum arabic under the name of Persian gum (Dymock, Pharm. J. [3] 9, 145).

ALOUCHI RESIN *v. Aluchi resin*, art. RESIN.

ALPHOL *v.* SYNTHETIC DRUGS.

ALPINIA OFFICINARUM *v.* GALANGA ROOT.

L.E.S. 7 39168

ALPINIA OIL. An essential oil obtained from the leaves of *Alpinia malaccensis*; sp.gr. 1·02 at 26°, rot. power +6·5°. Consists mainly of methyl cinnamate, together with *d*-pinene (Van Romburgh, Proc. K. Acad. Wetensch. Amsterdam, 1900, 3, 451).

ALPININ *v.* GALANGA ROOT.

ALPOGADA *v.* ALOO BOKHARA.

ALQUIFON. Black lead ore or Potters' ore. A native lead sulphide, used by potters to glaze coarse ware.

ALSOL *v.* SYNTHETIC DRUGS.

ALSTONIA BARK. The bark of *Alstonia constricta* (F. Muell.), an apocynaceous tree growing in Australia. It has a bitter taste, slightly camphorous odour, contains a neutral bitter principle (similar to *cailcedrin* and *tulucumin*), a volatile oil smelling like camphor, an iron-greening tannin, resin, fat, wax, a protein-like substance, oxalic and citric acids (Palm, J. 1863, 615).

Müller and Rummel (Chem. Soc. Trans. 35, 31) obtained a yellow substance to which they gave the name *alstonine*. Oberlin and Schlagdenhauffen (Pharm. J. [3] 10, 1059; Chem. Soc. Abstr. 38, 127) showed that this body consisted of two compounds *alstonine* and *alstonicine*, the former being soluble in acids with fluorescence, the latter without.

Hesse subsequently (Ber. 14, 264; Annalen, 205, 360) isolated:

Alstonine (chlorogenine) $C_{20}H_{21}N_2O_4$, a brown amorphous mass, a strong base, soluble in chloroform, alcohol, and sparingly soluble in ether, and melting when anhydrous at 195° (uncorr.)

Porphyrine $C_{21}H_{25}N_3O_2$, a white powder melting at 97° (uncorr.), soluble in alcohol, chloroform, ether, and acids, with blue fluorescence.

Porphyrosine, soluble in acetic acid, forming a pink solution.

Alstonidine, colourless needles, melting at 181° (uncorr.), soluble in chloroform, ether, alcohol, and acetone.

Hesse, however, could not find a trace of quinine (Ber. 11, 1546, 1753).

ALSTONIA SPECTABILIS. *Poelé bark.* Contains *alstonamine* (Hesse, Ber. 11, 1548), and the alkaloids of dita bark. It contains six times as much echitammonium hydroxide as dita bark (Hesse, Annalen, 203, 144).

Its physiological action is like that of curare.

ALSTONITE. A rare mineral consisting of barium and calcium carbonate $(Ba,Ca)CO_3$, crystallising in the orthorhombic system. The small crystals have the form of acute six-sided pyramids, and consist of complex twin intergrowths. Found in 1834 in a lead- and zinc-mine near Alston in Cumberland, and in 1909 in a coal-mine near Durham. L. J. S.

ALTI. Indian name for a root used at Goa as a substitute for Althæa (Dymock, Pharm. J. [3] 8, 101).

ALUDEL. The aludels of the earlier chemists were pear-shaped pots generally made of earthenware, but sometimes of glass, open at both ends. Each aludel had a short neck at the top and bottom, so that a series of them could be fitted together by means of the necks. The earthenware pear-shaped vessels in which the mercurial vapours are condensed at Almaden in Spain are also known as aludels.

ALUM *v.* ALUMINIUM.

ALUMINATES *v.* ALUMINIUM.

ALUMINIUM. Sym. Al. At. wt. 27·1.

Occurrence.—Aluminium is the most widely distributed element in nature with the exception of oxygen and silicon. It is not found in the metallic state.

As oxide, Al_2O_3, aluminium is found in *corundum*, or, coloured by metallic oxides, in *sapphire*, *ruby*, *emery*, &c. The hydrated oxide Al_2O_3,H_2O occurs as *diaspore*, and, together with ferric oxide, silica, &c., as the important mineral *bauxite*.

Aluminium occurs in combination with oxygen and metals as *aluminates*, in *spinel* $Al_2O_3{\cdot}MgO$, *chrysoberyl* $Al_2O_3{\cdot}BeO$, *gahnite* $Al_2O_3{\cdot}ZnO$. As hydrated sulphate it is found in *aluminite* or *websterite* $Al_2O_3SO_3,9H_2O$, and as *alunogen* $Al_2O_3(SO_3)_3,18H_2O$; as the double sulphate of aluminium and potassium in *alumstone* or *alunite*; and, as an efflorescence on aluminous minerals in the form of the alums of potassium, sodium, ammonium, &c.

Aluminium occurs principally, however, as silicate in the various *clays*; as silicate containing silicon fluoride in the *topaz*; and, as double silicate, with iron, magnesia, lime, &c., in *garnets*; with potassium, sodium, magnesium, and calcium in immense quantities in the varieties of *felspar*.

As double fluoride of aluminium and sodium it is found in *cryolite* $Al_2F_6{\cdot}6NaF$; as hydrated phosphate in the *turquoise* and in *wavellite*, and as borate in a crystalline mineral occurring in Siberia.

Although present in such quantities in the soil, aluminium is not usually considered a constituent of the ash of plants except of cryptogams; Yoshida, however (Chem. Soc. Trans. 1887, 748), has found it in a number of phanerogams in Japan.

History.—The name of this metal is derived from *alumen*, a term applied by the Romans to all bodies of an astringent taste. Pott, in 1746, stated that the basis of alum is an argillaceous earth; and in 1754 Marggraf pointed out the distinction between alumina and lime, and its presence in combination with silica in clay.

Davy, in 1807, having isolated the alkali metals by electricity, endeavoured, unsuccessfully, to reduce alumina in the same manner.

Oersted, in 1824, prepared aluminium chloride by passing chlorine over a mixture of alumina and carbon heated to redness. He appears to have reduced the chloride to the metallic condition by heating with potassium amalgam: (Berzelius, Jahresb. 1827, [6] 118). The amalgam produced oxidised rapidly in the air, and left, on volatilising the potassium, a tin-white metal.

Wöhler, in 1827 (Annalen, 1828, 37, 66), having failed to procure the metal by Oersted's method, obtained it by the decomposition of the *anhydrous* chloride with potassium, as a grey powder, which became brilliant under the burnisher.

Bunsen and Deville, in 1854, independently, obtained the metal by electrolysis of the fused chloride. Deville, in the same year, much simplified the manufacture by substituting sodium for the more expensive potassium. In 1854 he was installed in the manufactory of Javel by the Emperor Napoleon III., and supplied with the necessary apparatus for experiments

on the large scale. Afterwards his process was removed to Nanterre and finally to Salindres. A description of his method is given in Ann. Chem. Phys. [3] 43, 5–36, and specimens of the metal produced were shown at the Paris Exhibition of 1855.

Shortly after the publication of these results, Messrs. Dick and Smith, under the direction of Dr. Percy, prepared aluminium by the action of sodium on the then newly discovered mineral *cryolite*, some of the product being shown by Faraday at the Royal Institution in March, 1855 (Phil. Mag. 10, 365).

About six months subsequently, Rose, independently, prepared it in the same manner, and published his results in an extended article in P. 96, 152 (Phil. Mag. 10, 233).

Deville at once turned his attention to this process (Ann. Chim. Phys. [3] 46, 451); but on account of the impurity of the metal produced, he preferred the double chloride of aluminium and sodium, using cryolite as a flux only.

The first manufactory in England was started at Battersea, London, in 1859, by F. W. Gerherd. Some of his metal was shown at the Society of Arts Exhibition in 1860. Messrs. Bell, of Newcastle, also prepared aluminium and aluminium bronze in 1863, using Netto's process. A mixture of 200 lbs. of cryolite and an equal weight of common salt was brought to fusion, and 40 lbs. of sodium gradually added. The charge thus contained only 5 p.c. of aluminium, but less than half of this was obtained in the yield.

The manufacture ceased in 1874. In Grabau's process (J. Soc. Chem. Ind. 1891, 433) aluminium fluoride was subjected to the action of metallic sodium. Other modifications were proposed from time to time, but the production of aluminium made no notable advance. Weldon, in 1883, summed up the position of the industry in the statement that 'the only method known for the manufacture of aluminium is Deville's. M. Pechiney has improved and cheapened the modes of working, and the appliances for carrying that method into effect, but this is all the progress which has been made in the manufacture of aluminium during the last five and twenty years.'

When the great stability of the available compounds containing aluminium is considered, it is not to be wondered at that the many attempts that have been made to prepare the metal by the action of the usual reducing agents, such as carbon, hydrogen, or hydrocarbons, have met with so little success. The heat of formation of these compounds is an index to their stability, and may be taken as a measure of the energy requisite for the isolation of the aluminium. The operation is not likely to succeed unless the elements which become separated from the aluminium enter into new combinations of still greater stability. The nature of the changes that might be expected to take place may be expressed in the following equations:—

$$2Al_2O_3 + 3C = 4Al + 3CO_2$$
or $$Al_2O_3 + 3C = 2Al + 3CO$$
$$Al_2O_3 + 6H = 2Al + 3H_2O$$
$$Al_2O_3 + 6Na = 2Al + 3Na_2O$$
$$Al_2Cl_6 + 6H = 2Al + 6HCl$$
$$Al_2Cl_6 + 6Na = 2Al + 6NaCl$$
$$Al_2F_6 + 6Na = 2Al + 6NaF.$$

In order that there may be a likelihood of these reactions occurring, the heat arising from the formation of the compounds on the right hand should exceed the heat concerned in the decomposition of the aluminium compounds on the left. The following table will show how far this is the case:—

	Calories		For amount equivalent to 2Al
Al_2O_3	391,600	$\frac{3}{2}CO_2$	145,500
		3CO	86,400
		$3H_2O$	174,900
		$3Na_2O$	302,700
Al_2Cl_6	323,600	6HCl	132,000
		6NaCl	587,400
Al_2F_6	558,000	6NaF	604,200

It will be seen that only the last two reactions will be at all likely to take place, and these heat values indicate that sodium is a much more favourable reagent than carbon or hydrogen, and that the highest excess of heat evolved over that absorbed occurs in the case of the aluminium chloride in presence of sodium.

The following analyses, taken from Hoffmann's Ber. Entwick. Chem. Ind. (1) 603, show the composition of commercial aluminium as produced under Deville's process:—

	1	2	3	4	5	6	7	8	9	10
Locality	Paris	Paris	Berlin	Paris	Paris	Paris	Bonn	Nanterre (Morin)		
Analyst	Salvétat	Salvétat	Mallet	—	Dumas	Dumas	Kraut	Kraut	Kraut	Sauerwein
Aluminium	88·35	92·97	96·25	92·60	92·5	96·16	94·7	—	—	97·2
Silicon	2·87	2·15	0·45	0·45	0·7	0·47	3·7	0·04	0·12	0·25
Iron	2·40	4·88	3·29	7·55	6·8	3·37	1·6	1·62	2·26	2·40
Copper	6·38	—	—	—	—	—	—	—	—	—
Lead	trace	—	—	—	—	—	—	—	—	trace
Sodium	—	trace	trace	—	—	—	—	—	—	—

Moissan has shown (Compt. rend. 121, 851) that it contained also from 0·1 to 0·5 p.c. of sodium; 0·3 to 0·4 p.c. of carbon and other impurities. These impurities would have a very considerable effect on the properties of the metal, and any statements based on observations with such metal, or even with the metal now being made, must be accepted with caution.

The production even in 1885 was small and did not exceed 2½ tons at Salindres and 2½ cwt. in the United States.

According to Mallet, pure aluminium may

be prepared by the method adopted by him in his determination of the atomic weight of that element (Phil. Trans. 171, 1018). Ordinary commercial aluminium is converted into bromide by the direct action of bromine. On account of the violence of the action, the metal should be immersed only for a short time, at intervals, until dissolved, or should be added in very small pieces. The bromide so produced is freed from bromine by distillation and fractionally distilled, that portion boiling uniformly at 263·3° being reserved. This portion is colourless, entirely soluble in water, and consists of the pure bromide.

It is heated with sodium (which has been carefully freed from oil and well scraped) in a crucible made of a mixture of pure alumina and sodium aluminate. The amount of sodium used should not be sufficient to reduce the whole of the bromide, or the aluminium is liable to contain sodium. The globules of metal are fused together before the blowpipe on a bed of alumina, immersed for a short time in hydrochloric acid, washed and dried. Pure aluminium might also be produced by the electrolysis of the pure bromide or chloride.

The purification from metallic impurities on the large scale involves many difficulties. The only method of obtaining satisfactory metal is to ensure as high a state of purity as possible in the first instance by making use of selected materials and avoiding contamination in the process of manufacture.

By the establishment of Deville's process the price of aluminium had been brought down from 18*l.* per lb. to 1*l.*, at which it stood till 1887.

The double chloride of sodium and aluminium used contained only 14 p.c. of aluminium, and the working of large charges with a small yield together with the high cost of sodium and fuel stood in the way of any prospect of reduction in the price of the metal.

The introduction of Castner's process, by which sodium could be produced much more cheaply, led to the establishment of the Aluminium Company's works at Oldbury, and effected some reduction in the price of aluminium. Meanwhile Messrs. Cowles (Patents Aug. 18, 1885, and Jan. 26, 1886) brought electrical heating into operation, and, though their process was not adapted to the production of aluminium, it was capable of furnishing alloys of aluminium with copper and other metals. These could be made at one-tenth the price which had ruled for aluminium, and the valuable properties of aluminium bronze, Hercules metal, and other alloys were soon recognised. Moreover, the discovery of the effect of the addition of minute amounts of aluminium to iron and steel gave a further stimulus to the production of aluminium. C. W. Siemens had already described an electric furnace (1881) capable of giving very high temperatures, and the type of furnace patented by Messrs Cowles Bros. was based on similar lines.

The furnace is a rectangular box, one foot wide, five feet long, and fifteen inches deep, all inside measures. Two carbon electrodes pass through pipes in the ends; they are three inches in diameter and thirty inches long; this size could not be exceeded, as larger carbons disintegrated under the intense heat. For a non-conducting furnace lining, fine particles of charcoal are washed in lime-water, exposed to the air and dried. They thus become coated with lime and are of good insulating power. At the high temperature produced, ordinary charcoal becomes converted into graphite and forms a good conductor. The two electrodes being within a few inches of one another, the charge of twenty-five parts of corundum, twelve parts of carbon, and fifty parts of granulated copper is placed around and between them, covered with small lumps of charcoal, and the whole covered with an iron top lined with fire-brick. The current from a powerful dynamo is then passed, and the electrodes moved if necessary to produce the requisite resistance. In about ten minutes, the copper having melted between the electrodes, the distance between them is increased while the current is raised to 300 amperes of fifty volts E.M.F. and the yield 1 lb. per E.P.H. hour. As the resistance is increased, the temperature rises, the alumina is reduced to the metallic condition and alloys with the copper, while its oxygen forms carbon monoxide and burns at the openings in the cover with a white flame. After about five hours the operation is completed. The alloy produced is brittle, consisting of copper and 15 p.c. or upwards of aluminium. When boron or silicon oxides have been added, the bronzes produced contain these elements. It is melted, cast into ingots, the percentage of aluminium determined, and sufficient copper added to produce 'aluminium bronze,' or the required alloy.

When other metals, such as iron, nickel, silver, &c., are substituted for copper, corresponding alloys are produced.

The slag produced is hard and compact, but soon falls to a fine alkaline powder; it contains alumina, calcium aluminate, with traces of copper, silicon, &c.

Pure aluminium cannot be produced satisfactorily by this method, as it remains, to a great extent, mingled with the carbon.

See further, W. P. Thompson (J. Soc. Chem. Ind. 1886, 206); Mabery (Amer. J. Sci. 308, and Amer. Chem. J. 1887, 11).

The Electrical Process.—A new principle was, however, introduced into metallurgy, and the application of electricity for purposes of heating and reduction of metals has made rapid progress in recent years. Its full development had not, however, been reached in the process just described. It had been shown that, though the fusion of a substance like alumina could not be economically effected owing to its high resistance, the addition of copper and other metals enabled the furnace charge to conduct the current. If a suitable solvent could be found for alumina then the electrolytic action of the current could be brought into play. When this was accomplished the chemical method of decomposition would give place to the electrolytic method, and the isolation of aluminium become a question of a sufficient current at the necessary voltage. This voltage can readily be calculated from the heat of formation of the compound in question by dividing the number of calories per equivalent by 23,250. We thus obtain for alumina 2·81 volts, for

aluminium chloride 2·32 volts, for aluminium fluoride 4·00 volts, for aluminium sulphide 0·9 volt.

A suitable solvent is found in native cryolite $3NaF{\cdot}AlF_3$, which may be brought to fusion below 1000°, and will dissolve 15 to 20 p.c. of its weight of alumina, and in this condition it is likely that the voltage is somewhat lower—in the case of alumina about 2·3 volts.

In the year 1886 the Héroult process was patented and soon came into use at Neuhausen, and at the Société Electrométallurgique at Froges, near Grenoble. In this process the anodes consisted of carbon and the cathode was the carbon lining of the furnace, the distance between the anode and cathode being capable of adjustment by raising or lowering the anode. The cryolite was first melted in the bath by utilising the heat generated by the resistance to the electric current, and then alumina was added, and the additions continued from time to time as the bath became exhausted. The metallic aluminium settled at the bottom of the bath in the neighbourhood of the cathode, and was tapped every 24 hours.

The purity of the metal at first was 97–99 p.c. There were at disposal 360 kilowatts at Froges, and just over 1000 kilowatts at Neuhausen (J. Soc. Chem. Ind. 1892, 910); the yield usually obtained was about 1¼ lbs. of aluminium per kilowatt-day, an efficiency of less than 25 p.c.

The Hall process, brought out in the United States about the same time, only differed from Héroult's in matters of detail, the anodes being rods of carbon 3 inches in diameter, or of larger dimensions in sections banded together, the electrolyte being alumina dissolved in mixed fluorides of calcium and aluminium or $AlF_3{\cdot}NaF$.

Minet (Compt. rend. 112, 231) used a bath composed of 62·5 p.c. of common salt and 37·5 p.c. of cryolite, but his metal seems to have contained 2 to 3 p.c. of impurity, which was chiefly silicon, owing largely to the impurity of the alumina used by him. Aluminium so prepared was liable to contain sodium, owing to the fact that the voltage necessary for the decomposition of aluminium fluoride differed so little from that required to decompose sodium fluoride—viz. 4·7 as against 4.

There was added to the bath as the operation proceeded, a mixture of hydrated alumina, cryolite, and alumina dissolved in cryolite.

Kleiner invented a furnace for the decomposition of cryolite, and carried on the production of aluminium at Tyldesley in Lancashire; a plant was also operated on the lines of the Héroult system at Patricroft near Manchester.

In this case the dynamos were run by steam power, and it soon became manifest that this could not compete with advantageous supplies of water power which began to be called into requisition wherever such power was available.

Mention should also be made of the method of Bucherer, D. R. P. 63995 (1892), who prepared aluminium by electrolysing the double sulphide of aluminium and an alkali or alkaline earth, the chief obstacle to success being the expense and difficulty attending the production of the sulphide.

It soon became evident that the Hall and Héroult process must hold the field, and that coal could not compete with cheap water power in this industry, and rapid expansions of the industry were made. The price had by 1891 been brought down to one-fifth of that which had ruled under Deville's process, and the production had increased to over 300 tons per annum. The accompanying statement is the cost of production at this period, as given by A. E. Hunt (Eng. and Mining Journ. 1891, 280). For 1 lb. of aluminium there was requisite

2 lbs. alumina	costing	6	cents
1 lb. carbon electrode	,,	2	,,
Chemicals, pots, &c.	,,	1	,,
22 E.H.P one hour	,,	5	,,
Labour, interest, repairs	,,	5	,,

making 19 cents in all.

The following firms were at this period manufacturing either aluminium or its alloys:—

In England—
- Cowles Syndicate (Cowles process).
- Reduction Syndicate (Hall process).

In the United States—
- Pittsburg Reduction Company.
- Cowles Electric Smelting Company.
- United States Aluminium Metal Co.

On the Continent—
- Société Electrométallurgique at Froges.
- Aluminium Industrie Actien-Gesellschaft at Neuhausen.

Further progress was mainly in the direction of increasing the yield and bringing down the cost of production whilst perfecting the various details of the process so that a purer product could be made.

We shall now describe the further development of the industry and the manufacture as it stands to-day after over 20 years of experience; and in doing so it will be well to consider in greater detail (*a*) the production of alumina, (*b*) the making of the carbon electrodes, (*c*) the nature and arrangement of plant, including the reduction furnaces.

Development of the Aluminium Industry.—The first factory established on electrical lines was that started in 1888, at New Kensington, by the Pittsburg Company, which is now known as the Aluminium Company of America, and conducts operations at the Niagara Falls, the Shawingian Falls, and at Massena.

Amongst the pioneers of the industry were also (1) Aluminium Industrie Aktien-Gesellschaft, who control works at Neuhausen, Rheinfelden, and Lend Gastein; (2) the British Aluminium Company, with reduction works operating in 1896 at Foyers and now at Kinlochleven (Argyllshire), and branch works at Greenock, Larne, and Milton (Staffordshire),—this company is also associated with reduction works at Stangfiord (Norway), and projected works at Orsières (Switzerland); (3) Société Electrométallurgique Française at Froges, La Praz, and St. Michael, and the Cie. des Produits Chimiques d'Alais et de la Carmargue.

There are also works on a smaller scale under the Aluminium Corporation at Wallsend, with construction going on at Dolgarrog (N. Wales), the Anglo-Norwegian Company at Vigeland Falls (Norway), and developments in Italy at Bussi. The cost of production of the metal to-day is said to be 61*l.* per ton as a minimum, though at most works it would reach 80*l.* (Mining World, June 26, 1909).

The market price of aluminium ingots in 1902–4 was 120*l.* per ton, but it rose to 200*l.* in 1906, and has since then fallen to 65*l.* (1909), though it is now again advancing. Since 1902 no trustworthy record has been made of the world's output of aluminium. It remained, however, fairly stationary in the neighbourhood of 8000 tons from 1900 to 1905 inclusive, and since then has grown steadily, and may be estimated for 1909 at 30,000 tons. In the United States Geological Survey publications (Metallic Products) for 1908 there may be found the estimated consumption of metal in the United States, from which it appears that in 1907 this amounted to nearly 7700 tons, and in 1908 to nearly 5000 tons.

The following is a statement of the production of aluminium in metric tons from 1889 to 1899, (*a*) in the United States, (*b*) total output :—

	a	*b*
1889	22	93
1890	28	193
1891	68	302
1892	118	505
1893	154	870
1894	250	1491
1895	417	1835
1896	591	2250
1897	1814	5220
1898	2359	6860
1899	2948	8950

The Production of Alumina.—The raw material from which the alumina is usually made is bauxite, deposits of which occur at Beaux and in the Var (S. France), at Feistritz (Austria), Wochein (Styria), Irish Hill (Ireland), Georgia, Arkansas, Alabama (United States), and in New South Wales. The physical condition of the bauxite varies considerably, so that some kinds are more readily acted upon for the production of alumina than others. In the aluminium industry a low content of iron and silica is desired, especially the latter; it is therefore usually found advantageous to employ the red bauxites, the white bauxites being used preferably in the manufacture of sulphate of alumina. The following table gives the composition of typical samples :—

Locality	Beaux		Var		Wochein		Feistritz			Irish	Georgia
			Red	White	Dark coloured	Light coloured	Reddish brown	Yellow	White	Raw	
Al_2O_3	60	75	50–62	65–74	63·16	72·87	44·4	54·1	64·6	35·0	60·5
Fe_2O_3	25	12	24–28	0·3–3	23·55	13·49	30·3	10·4	2·0	38·0	1·9
SiO_2	3	1	1–7	12–18	4·15	4·25	15·0	12·0	7·5	3·5	3·3
H_2O	12	12	12–13	14	8·34	8·50	9·7	21·9	24·7	21·5	32·1
TiO_2	—	—	0·1–4	—	trace	trace	—	—	—	2·0	2·2

The following analyses by Leop. Mayer and O. Wagner (Dingl. poly. J. 248, 213) show that the appearance of bauxite cannot be relied on as a criterion of its value. The origin of the samples is not given :—

	Appearance	Hygroscopic moisture	Combined water	Al_2O_3	Fe_2O_3	SiO_2	MnO_2	CaO	MgO	P_2O_5
1	Pure white	2·33	13·86	29·80	3·67	44·76	—	2·75	0·84	1·47
2	Yellow	1·03	27·85	43·22	14·39	10·43	—	1·61	—	1·13
3	,,	1·30	27·70	50·38	11·68	8·34	trace	trace	trace	0·61
4	Red	1·34	23·12	33·86	25·69	12·41	2·42	trace	—	0·53
5	,,	1·31	23·81	46·18	22·05	4·82	—	0·89	—	0·66
6	,,	0·95	20·83	62·10	6·11	5·06	2·01	3·20	trace	trace
7	,,	1·17	4·75	21·80	3·75	60·10	—	6·06	2·49	trace

The amount of bauxite mined in 1907 was 260,000 tons, three-fifths of which was produced in France.

For the manufacture of the purest form of alumina the bauxite is first roughly powdered and calcined to get rid of water and any organic matter. It is then more finely ground and introduced gradually with agitation into kiers containing caustic soda solution of 1·45 sp.gr. The kiers are now closed and the charge heated for some hours under high-pressure steam—about 70–80 lbs. The contents of the kiers are then transferred to the filter presses, and the filtrate further cleared through wood pulp in lead-lined vats. The liquor contains essentially sodium aluminate, which may be decomposed by passing carbon dioxide into it, but it is now more usual to adopt the Bayer method of precipitating the alumina. This method depends on the fact that the addition of alumina effects the decomposition of the aluminate and throws down some 70 p.c. of the alumina. The dissolved liquor now contains alumina and soda in the proportion $Al_2O_3 : Na_2O :: 1 : 6$. The precipitated hydrate of alumina is allowed to settle, and the liquor with its undecomposed portion is run off into weak-liquor tanks. The hydrate is filter-pressed, sufficient being left in the vat to serve as precipitant for the next charge. The weak liquor may, after concentration, be used over again for reacting upon a further amount of bauxite.

The hydrate of alumina so obtained ought to contain less than 1 p.c. of mineral impurity, sodium and silicon being the more objectionable impurities. To bring it into a suitable physical

condition for use in the reduction furnaces it must be calcined at 1100°–1200°, so that it shows no tendency to give up moisture when used in the furnace or to absorb moisture when exposed to air.

The alumina of to-day is superior to that of fifteen years ago, and the cost of production less than one-half. It constitutes, however, about one-fifth of the whole cost of manufacture of aluminium, and many processes have been brought forward with a view to improve or cheapen the product. Of these may be mentioned the patents of Penokoff (Eng. Pat. Nov. 19, 1895, Mar. 18 and May 13, 1896, &c.). Endeavours have been made to obtain alumina of sufficient purity from bauxite, clay, felspar, or kaolin by electrically heating them with iron (or its oxide), carbon and cryolite, thus separating ferrosilicon from alumina; Moldenhauer (J. Soc. Chem. Ind. 1909, 148), Sinding-Larsen (*ibid.* 1908, 409), and Tone (Electrochem. and Metallurg. Ind. 1909, 35), Hall (J. Soc. Chem. Ind. 1902, 49). Recently Serpek has proposed to prepare alumina by forming the carbide and acting upon this with producer gas consisting of 77 p.c. nitrogen, 23 p.c. carbon monoxide, and a little carbon dioxide. He claims that a tolerably pure nitride of aluminium is formed, and this decomposed by steam yields alumina and ammonia (Journal du Four Electrique, 315, 1; J. Soc. Chem. Ind. 1911, 26; Fr. Pat. 405712 and 418059).

The Making of Carbon Electrodes.—Bituminous coal, anthracite, retort carbon, natural or artificial graphites, soot and oil-coke are all materials which have from time to time been used in the production of carbon electrodes. In deciding which of these materials should be used, account must be taken of: (*a*) Supply and cost of raw material; (*b*) ash content; (*c*) amount of volatile matter and sulphur; (*d*) conductivity for electricity and heat. It must also be understood that electrodes used for the production of aluminium differ in character from those used for lighting or for the production of calcium carbide and many other purposes where graphitisation of the carbon is an advantage and the presence of mineral matter is quite permissible and even necessary. The graphitisation of amorphous carbon is indeed effected by exposing it to a high temperature under electrical heating after admixture with finely divided iron.

It is said that at the temperature employed the iron volatilises. Be this as it may, the ash of such carbon contains a considerable amount of oxide of iron. Aluminium, boron, silicon, and other elements which form carbides can be used as graphitising agents, as also to some extent the oxides of these elements.

It may be taken that, so far as it is capable of reduction in the aluminium furnace, the mineral ash contained in the carbon alloys itself with the aluminium, as also the foreign matter present in the alumina. The amount of alumina used should be about double that of the aluminium resulting therefrom, and the electrode consumption about two-thirds of the aluminium, so that an estimate may be made of the impurity as silicon contained in the metal. Assuming the silica in the alumina and in the electrode as 0·3 p.c., in each case, the amount of silicon in the metal will be that contained in 0·8 p.c. of silica, *i.e.* 0·37 p.c.

The electrical resistance is in microhms per cubic inch of

	0°	1000°
Amorphous carbon (pressed)	1·63	1·45
Graphitic carbon . .	0·42	0·25
Electrodes for aluminium .	3·00	2·60

The resistance per cubic centimetre would be 2·54 times these values. (For further detail, The Electric Furnace, Stansfield, or the pamphlet issued by the Acheson Graphite Co., may be consulted.) In addition to low resistance to the electrical current, it is desirable that electrodes should be of low conductivity for heat, that they should be sufficiently hard and resistant to superficial oxidation, of low porosity and of even character throughout their whole mass.

To produce electrodes having these qualities the material (oil-coke is largely used) must be carefully selected, ground, calcined, and subjected to high pressure with the admixture of tar or other material to act as binder. They are then baked at a temperature of about 1200°. in a kiln, in principle resembling a pottery kiln, the surface of the blocks being protected from oxidation by being embedded in carbon. The permissible current-density for good electrodes of this type is 25 to 60 amperes per square inch of transverse section, though in practice a much lower current-density is employed. For further details and description of Mendheim and other kilns suitable for baking the blocks, reference may be made to Die Künstlichen Kohlen, by Julius Zellner. The connection of the carbon blocks with the anode beam carrying the current may be effected by means of an iron claw let into the block or a copper hanger fitted into it by a screw contact.

The Reduction Furnaces.—These consist essentially of an iron casing lined with carbon, the general character and arrangement of which is shown in transverse section (p. 108). The electrodes vary in size and form in different works, and are not necessarily arranged in two rows as indicated in the figure. Their total sectional area is, however, always adapted to the current to be used and good electrodes will act satisfactorily under a current-density of 8 to 10 amperes to the square inch. The lower part of the carbon body serves as the cathode, and a special form of cathode is let into the carbon at the base of the furnace. In starting a furnace it is usual to introduce first the cryolite, which is brought to a state of fusion by electrical heating. Alumina is then fed in gradually at the surface of the cryolite, and as it dissolves the resistance gradually falls to about 5 or 6 volts, and the temperature of the bath will be generally 1000°. The electrolytic action brings about a decomposition, which has been usually taken to result in the formation of carbon monoxide, according to the equation

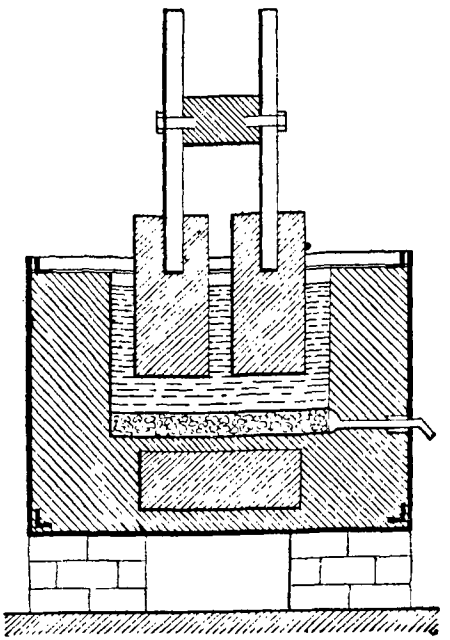
$$Al_2O_3 + 3C = 2Al + 3CO,$$

but there is little doubt that primarily carbon dioxide is formed, and the change should be expressed as

$$2Al_2O_3 + 3C = 4Al + 3CO_2.$$

In the former case the carbon used would be two-thirds of the weight of the aluminium

produced, whilst in the latter it would be one-third. In practice the ratio of carbon to aluminium lies between these extremes.



The production of aluminium is discontinuous, for about 2 hours after the proper charge of alumina has been added the voltage of the furnace rises rapidly and affords an indication that more alumina must be added. The aluminium collects at the bottom of the bath of electrolyte, and is tapped off at stated periods, either every day or at longer intervals. The reduction of alumina by electrolytic methods on a laboratory scale is beset with difficulties; an account of experiences in this direction is given in papers by Neumann and Olsen (Met. and Chem. Engineering, 1910, 185), and Tucker (*ibid.* 1909, 315).

Physical Properties.—Commercial aluminium is a metal with the whiteness of tin. It has been obtained in crystals resembling octahedra, and is very slightly magnetic.

Its specific heat is, at

−100°	0·1893	300°	0·2434
0°	0·2098	500°	0·2739
100°	0·2236	650°	0·3200

(Schmitz, Proc. Roy. Soc. 72,177).

The total heat required to bring a kilogramme of aluminium from 0° to 625° is 239,400 cals., and its latent heat of fusion is 80. It melts at 654·5° (Heycock and Neville), 657·3° (Holborn and Day), the melting-point being dependent (as are other physical properties) on its purity. Small amounts of silicon and iron, which are always present, have a considerable effect on its behaviour, both physically and in contact with reagents. Lorenz found its conductivity for heat at 0° 0·3435, at 100° 0·3619; whilst Jaeger and Dresselhorst for metal containing 0·5 p.c. iron and 0·4 p.c. copper, found 0·4923 at 100°. Similarly the electrical conductivity of aluminium, taking copper as 100, is as follows: 98·5 p.c. purity, 55; 99 p.c., 59; 99·5 p.c., 61; 100 p.c., 66.

A sample of metal produced in 1856, having a lower degree of purity, gave 51·3.

Its elasticity modulus (*i.e.* load in kilogrammes per square millimetre, divided by its alteration in length) is 7462 as compared with 11,350 for copper, and the torsion moduli of these metals are 3350 and 4450 respectively.

The specific gravity of the molten metal is 2·54, and of the cast metal is about 2·66; this may be increased by rolling. Its expansion coefficient is 0·00002313 at 40° (Fizeau), and 0·0000315 at 600°. It expands on fusion to the extent of 4·8 p.c. (Toepler). In hardness it resembles silver, and the pure metal is softer than the impure. It becomes more elastic and also harder by hammering and rolling, and is capable of being drawn down to a wire of $\frac{1}{330}$ inch in thickness, or rolled into plate or beaten into foil to $\frac{1}{10000}$ inch thick. It can also be finely granulated for use in explosives, or prepared in the form of very fine powder, which is largely employed as 'thermite,' or as aluminium paint. The tensile strength of aluminium is 12 to 13 tons on the square inch, but this varies with the temper of the metal between 6½ and 15½ tons on the square inch, the elongation varying in the inverse manner from 23 p.c. to 1½ p.c. Aluminium has been largely used for overhead electrical transmission and it possesses many advantages for such purposes owing to its lightness. Its specific gravity being only $\frac{3}{10}$ of that of copper, and conductivity over 60 p.c., it follows that an aluminium cable has double the efficiency of a copper cable of the same weight as a means of conveying current. The tensile strength of aluminium is affected, of course, by its form, method of casting and mechanical treatment. Its ultimate strength in tons per square inch is in castings 7 tons, in sheet 11 tons, and in wire from 13 to 29 tons.

Although corroded in the atmosphere of some large towns, it is not more so than other metals used for cables, and under ordinary circumstances it merely becomes coated with a thin film of oxide which acts protectively.

There has been great difficulty in finding a wholly satisfactory solder for the metal, and one that shall resist corrosion. Dagger (J. Chem. Soc. Ind. 1891, 436) quotes as useful for heavy soldering Al 12 pts. Cu 8 pts. Zn 80 pts., and for light soldering Al 6 pts. Cu 4 pts. Zn 90 pts. Joints can, however, be made by autogenous welding with an oxyhydrogen or acetylene flame or electrically. Butt and other joints may be effected by various mechanical devices with the aid of fusion at the surfaces or by a casting of metal around the junctions.

Chemical Properties.—Aluminium absorbs about its own volume of hydrogen, which is, however, expelled on heating or *in vacuo*. It is practically unacted upon by oxygen at ordinary temperatures, but if finely divided it undergoes considerable oxidation at 400°, or even, though less rapidly, at lower temperatures. If of sufficient purity, water has no action upon it, though when sodium is present in the metal a slight action occurs. This is accentuated if copper, brass, or other metals are in contact with it. A recent use to which the metal has

been put is for the treatment of hard waters, which by intimate contact with the metal, are said to be softened and become less liable to form incrustation on the shell of the boiler. The halogen elements or acids readily act upon aluminium, and the chemical activity of the metal is such that a large amount of heat is generated on combination with these elements. The heat of formation of Al_2O_3 is 391,600 cals., Al_2S_3 is 124,400 cals., Al_2F_6 is 558,000 cals., Al_2Cl_6 is 323,600 cals., Al_2Br_6 is 243,900 cals., Al_2I_6 is 140,600 cals.

The very great affinity which aluminium possesses for oxygen has been made use of in the application of 'thermite' as a means of reducing oxides. Goldschmidt, D. R. P. 96317 (1895), has thus used the finely divided metal in the production of iron, manganese, chromium, nickel, cobalt, titanium, boron, molybdenum, tungsten, vanadium, and other metals.

Reagents which readily part with the halogens, such as $SiCl_4$ and PCl_3, also attack it, and carbon or the oxides of carbon at high temperatures convert it into carbide, Al_4C_3. Concentrated nitric acid has very little action upon it unless the metal is impure, but more dilute acid dissolves it appreciably. Sulphuric acid only reacts if hot and concentrated, and in these circumstances there is a considerable evolution of sulphur dioxide. Alkalis or the hydroxides of the alkaline earths, especially baryta, attack the metal, and hence vessels used for culinary purposes will be corroded if brought into contact with soda. Mallet (*Chem. Soc. Trans.* 1876, 340) found that molten aluminium is acted upon by nitrogen with the formation of nitride.

If brought into intimate contact with mercury in presence of moisture, aluminium is readily converted into the hydroxide, and when exposed to the vapour of mercury with access of air, it undergoes rapid oxidation.

The action of organic acids on aluminium is inconsiderable. In presence, however, of sodium chloride these acids have a slight solvent action. Under like circumstances, tin and copper would be much more affected, with the production of injurious salts; the salts of aluminium are, however, quite harmless, and are almost entirely precipitated and rendered insoluble on boiling.

Perspiration, being acid, has no apparent effect; saliva, on account of its slight alkalinity, acts very slowly. Aluminium tubes have been used for insertion in the human body where much purulent matter was present, without perceptible corrosion.

Aluminium when fused with potash or soda is unaffected even at a dull red heat, but the superficial silicon is removed; metal so treated takes a good 'matt.'

Dry ammonia gas has no action; solution of ammonia has a slight action upon the metal, converting it into hydrate, whilst a portion passes into solution.

Pure aluminium is less acted upon by most reagents than the commercial metal (Mallet).

For burnishing and engraving aluminium, the ordinary media are unsuitable. According to Mourey and others, an emulsion of equal parts of rum and olive oil is most satisfactory. The finish of manufactured articles is improved by a frosted appearance. This is produced by plunging the article momentarily into caustic alkali, washing well, and immersing in dilute nitric acid.

Action on metallic solutions.—Aluminium, especially in the form of foil, has a considerable action on many salts in solution. The action of sulphates and nitrates is usually very slow. All chlorides, except those of the alkalis and alkaline earths, are readily decomposed, even *aluminium chloride solution* dissolves the metal with evolution of hydrogen. Bromides and iodides have corresponding effects. The presence of chlorides in solutions of other salts much facilitates their action.

From a neutral or feebly acid solution of silver nitrate, silver is precipitated slowly; from an ammoniacal solution of the chloride, silver is rapidly precipitated as a crystalline powder.

From the nitrate or sulphate of copper, precipitation is slow, from the acetate quicker, and from the chloride or other salt in presence of sodium chloride, rapid and complete.

Mercurous salts are decomposed with formation of an amalgam. Lead and zinc are readily precipitated (*v.* also Cossa, Zeitsch. f. Chem. [2] 6, 380 and 443).

Action of dry salts and oxides.—The action of aluminium, when heated with certain salts and oxides, is peculiar, and shows, especially at high temperatures, the tendency of this metal to form aluminates.

It is not affected by potassium nitrate except above a red heat; it is then rapidly oxidised with formation of potassium aluminate. With alkaline carbonates combination takes place at a red heat with separation of carbon, and with alkaline sulphate combination takes place suddenly at redness with explosive violence; in both cases aluminates are formed.

When finely divided aluminium is mixed with oxide of copper, lead, or iron, combination takes place at a *white* heat only, with such violence as frequently to shatter the crucible. In the case of lead and copper oxides, aluminates are produced, and with iron an alloy of iron and aluminium (Tissier).

When heated with silicates or borates, aluminium liberates silicon or boron, forming an aluminate with the base. Fused silver chloride is reduced to metal; zinc is reduced from its fused chloride, whilst magnesium chloride is not affected (Flavitzky, Ber. 6, 195). The vapour of mercuric chloride is reduced with such energy by heated aluminium that the metal fuses.

Detection.—Compounds of aluminium, when heated, moistened with solution of cobalt nitrate, and again strongly heated produce a fine sky-blue colour (*Thenard's blue, q.v.*, art. COBALT).

Aluminium compounds are usually colourless. Silicates and other compounds insoluble in acids require to be finely powdered, mixed with 4 parts of sodium carbonate or fusion mixture, and heated strongly in a platinum crucible. The aluminium, having thus become converted into sodium aluminate, is dissolved out with hydrochloric acid, evaporated to dryness to render any dissolved silica insoluble, and treated with dilute hydrochloric acid. The aluminium is then present as chloride.

Aluminous solutions, on addition of an alkali,

give a white gelatinous precipitate of hydrate, soluble in excess of the precipitant and in acids. Ammonia produces the same precipitate, which is only slightly soluble in excess, and is entirely reprecipitated on boiling off the excess of ammonia if sufficient ammonium chloride be present,

Estimation.—Aluminium is always precipitated as the hydrated oxide $Al_2O_3,3H_2O$.

For this purpose the solution, which, in presence of alkalis or alkaline earths, is mixed with excess of ammonium chloride, is treated with a *slight* excess of ammonia, and the solution boiled until the free ammonia is expelled. The hydrate, having thus become totally precipitated, is filtered, well washed, dried and heated in a platinium crucible, the heat being finally raised to bright redness for five minutes over the blowpipe. The weighed residue consists of anhydrous oxide, Al_2O_3, and contains 53 p.c. of aluminium. The separation from other metals is not difficult. The heavy metals may be precipitated from the *acid* solution by sulphuretted hydrogen, leaving the aluminium in solution, whilst the precipitation in presence of ammonium chloride in excess separates it from the alkalis and alkaline earths. From chromium and iron the separation is less simple. Chromium may be separated as follows:—The precipitated oxides are dried, mixed with 2 parts potassium nitrate and 4 sodium carbonate and fused in a platinum crucible. Alkaline chromate and aluminate are thus produced. The mass is digested with water and a small quantity of potassium chlorate and hydrochloric acid are then added, and the solution is evaporated to a syrup, with occasional addition of potassium chlorate to destroy the excess of hydrochloric acid and prevent its reducing action on the chromate. The aluminium in the diluted solution is precipitated as above by ammonia, leaving the chromate in solution.

For the separation from iron, the precipitated hydrated oxides are dissolved in the minimum quantity of hydrochloric acid and treated with an excess of *pure* strong potassium hydroxide solution, boiled for a few minutes, diluted, filtered, and well washed. The ferric oxide is thus precipitated and separated from the soluble alumina. The solution and washings are acidified with hydrochloric acid and precipitated by ammonia. On account of its solvent action upon glass, the treatment with potash should be performed in a porcelain dish, which is much less attacked, or, preferably, in one of silver.

Commercial Analysis of Aluminium.—The direct determination of aluminium, constituting as it does usually over 99 p.c. of the metal under examination, presents many difficulties. It has been proposed to estimate the aluminium by ascertaining the volume of hydrogen evolved on dissolving it in hydrochloric acid or the amount of chloride formed, but the errors to which such a determination is liable are too great to admit of sufficient accuracy; moreover, the impurities usually present give rise to corrections which detract from the simplicity of the method and complicate the result. The solution in caustic soda is preferable to this, the iron and copper remaining as a black residue, but the silicon, in part, at least, reacts with caustic soda, so that even in this case the hydrogen evolved cannot be taken as a measure of the aluminium present. In these circumstances it is customary to determine the impurities and arrive at the amount of aluminium by difference.

The impurities generally present in quantity are iron, silicon, and sometimes copper. Minute amounts of sodium, carbon, and nitrogen are also contained in the metal, but these should not greatly affect the result unless when dealing with specially impure metal. Commercially, therefore, iron and silicon alone are usually estimated. For the *iron*, the metal is dissolved in caustic soda, and this solution on acidulation with sulphuric acid yields sulphates of alumina and iron which redissolve in the acid, whilst the presence of copper is indicated by the appearance of a black residue. The amount of iron is finally determined by titration with potassium permanganate. For the *silicon*, the metal is digested with hydrochloric acid (in presence of nitric acid to avoid volatilisation of any silicon as chloride) forming a turbid solution owing to the separation of the silica. This is then boiled down with sulphuric acid until white fumes of this acid appear. The aluminium and iron salts are thus converted into sulphate, and redissolve on digestion with water, the silica being left in suspension.

After filtration and washing, the silica is strongly heated and weighed. *Copper* may be estimated as sulphide, or the black residue above mentioned may be dissolved and the copper estimated colorimetrically. If the amount of *sodium* is to be found, the metal must be dissolved in nitric acid to which a little hydrochloric acid is added. The solution is boiled down to dryness and exposed to a dull red heat so long as red fumes appear. The residue is extracted with water, care being taken finally to remove all alumina or other metals precipitated by the ordinary reagents. Ultimately the sodium salt remaining may be converted into sulphate and weighed as such. For fuller details a paper by Seligman and Willott may be consulted (Journ. Inst. Metals, vol. iii. p. 138).

For general analytical details, the following sources of information may be consulted: Moissan (Compt. rend. 121, 851); Gouthière (Analyst, 21, 270); Jean (Rev. Chim. Indust. 8, 5). The better qualities of commercial metal should not contain more than 0·5 p.c. of iron and silicon together, nor more than 0·03 p.c. of sodium.

Alloys.—The addition of quite small quantities of aluminium to certain metals (*e.g.* copper and iron) has a profound effect in modifying the properties of these metals. Likewise the addition of small quantities of certain metals (*e.g.* Fe, Mn, Si, &c.) to aluminium effects considerable change in the properties of this metal. The addition of 0·1 p.c. of aluminium to copper brings down its conductivity 23 p.c.; the addition of zinc, copper, nickel, iron, or manganese to aluminium is accompanied by considerable augmentation of the tensile strength. The alloys of aluminium may be classified into bronzes, casting alloys, and rolling alloys, according to their properties. The *true bronzes* consist of copper and aluminium alone, but there are many binary (and ternary) alloys which contain metals other than copper and yet sufficiently resemble bronze to be classed along with

it. The bronzes proper chiefly employed are gold bronze, containing 3 to 5 p.c. of aluminium; steel bronze, with 8·5 p.c. Al and some silicon; acid bronze, with 10 p.c. Al. The copper bronzes, with 90, 92·5, 95 and 97·5 p.c. of copper, are all good alloys, showing homogeneity and freedom from crystallisation. They are of great hardness and high tensile strength.

Such alloys possess very valuable properties, the ultimate stress of the 90 p.c. alloy being 38 tons to the sq. inch, and they have the further valuable property of being practically noncorrodible by sea-water; this property is also shown very markedly by bronzes containing manganese. These bronzes in hardness and tensile strength compare favourably with the best steel, and are similarly affected by tempering. The alloys high in aluminium and low in copper are also of great commercial value; a bronze with 4 p.c. copper by rolling and drawing showed a steady increase in tensile strength from 9·6 tons to 20 tons to the sq. inch.

A small percentage of manganese renders these alloys more ductile without reducing their ultimate stress, but large proportions of manganese increase the strength and lessen the ductility.

For further information reference may be made to the eighth report of the Alloys Research Committee of the Inst. Mech. Engineers (Carpenter and Edwards), and to the ninth report (Rosenhain and Lantsberry), also to The Metal Industry, 1909, 186 (Hiorns). The composition of other bronzes used industrially is given in the following table:—

	Al	Cu	Zn	Sn	Ni	Cr	Mg
Hercules bronze .	2	65	33	—	—	—	—
Chromium bronze .	95·75	4	—	—	—	0·25	—
Duralum .	79	10*	—	—	—	—	11
Partinium .	88·7	6·8	4·5	—	—	—	—
Grossmann's alloy .	87	8	—	5	—	—	—
Argentan .	7	70	—	—	23	—	—
Hercules metal (No. 3)	1·5	61	37·5	—	—	—	—

* Phosphorised copper.

The aluminium alloy containing 20–50 p.c. of copper or nickel is brittle, as is the alloy with 35 p.c. of manganese.

Rolling Alloys.—Aluminium alloys, containing 3 to 4 p.c. of copper or 1·5 to 5 p.c. of nickel, roll well, as do many other alloys containing copper and zinc, the former in small quantity, amounting to from 1 to 3 p.c., and the latter 10 to 12 p.c., or even more.

Magnalium consists of aluminium alloyed with 2 to 10 p.c. of magnesium. This alloy is lighter than aluminium, and in strength and workability equal to good brass.

Casting alloys are also largely used, consisting most frequently of aluminium, zinc, and copper in varying proportions (Richards, Eng, and Mining Journ. 1908, 715). Magnalium admits of introduction with advantage of small quantities of copper and nickel without unduly raising its specific gravity. The tensile strength and hardness of these alloys are considerable, and they are said to be resistant to atmospheric corrosion (Barnett, J. Soc. Chem. Ind. 1905, 832). Taps, tuyères, and the like are made from an alloy composed of aluminium, to which 12 p.c. Cd., 6 p.c. Cu, 5 p.c. Sn, 2 p.c. Ni are added. Pedestals are also made of aluminium, containing 14 p.c. Sb, 1·2 p.c. Cu, 12 p.c. Sn, 37 p.c. Zn, and 0·8 p.c. Pb; copper, with 10 p.c. Al and 1 p.c. Mn, is an excellent hard alloy for bearing metal or tool steel; horse-shoes are made from a ternary alloy of aluminium containing either 12 p.c. Cu and 10 p.c. Zn, or 5 p.c. Cu and 10 p.c. Sn. Aluminium or its alloys have proved useful where there is contact with concentrated nitric acid, or for stills and plant used in the sulphite pulp manufacture; also where stearic or other organic acids are dealt with. These alloys resist acid corrosion to a remarkable degree, and even if cooking utensils were made from an aluminium copper alloy, Carpenter and Edwards have shown that if corrosion does occur the copper is not dissolved out, and hence there is no danger of poisoning in using such vessels, since the salts of aluminium have no toxic action.

An improvement is effected by the addition of aluminium to *brass*. An alloy containing aluminium 2·5 p.c., copper 70 p.c., and zinc 27·5 p.c., is said to show nearly double the tenacity and considerably more than double the elongation of ordinary cast brass.

The presence of *tin* in aluminium renders it more fusible and brittle. According to Bourbouze (Compt. rend. 102, 1317), an alloy of aluminium 100 and tin 10 is strong, easily worked, may be soldered as easily as brass, is whiter and less affected by reagents than aluminium, and is very suitable for parts of optical instruments. Its sp.gr. is 2·85. The addition of aluminium to tin increases its hardness and tenacity. The alloys containing 5, 7, and 9 p.c. of aluminium are all easily worked and soldered. A larger proportion of aluminium is liable to separate out on melting.

Aluminium combines in all proportions with *cadmium*, forming malleable fusible alloys.

Small quantities of *silver* increase the hardness and elasticity and lower the melting-point without rendering aluminium brittle. The alloy containing 4 p.c. silver has been used for the beams of delicate chemical balances. When the addition exceeds 5 or 6 p.c. the metal becomes brittle; the 50 p.c. alloy is as hard as bronze, but very brittle. '*Tiers argent*' consists of 1 part silver and 2 parts aluminium; it is of considerable hardness, and is used for tablespoons, &c. The addition of 5 p.c. of aluminium to silver renders it as hard as standard silver and very permanent.

The presence of aluminium in *gold* considerably alters its properties. The addition of 0·186 p.c. of aluminium to *pure* gold increases the tensile strength from 7 tons to 8·87 tons per square inch, a greater increase than is produced by the same amount of any other metal (Roberts-Austen, Roy. Soc. Rep. April, 1888; Chem. News. 1888, v. 57, p. 133). With 1 p.c. aluminium the gold has the colour of 'green gold,' is hard but easy to work; with 5 p.c. aluminium it is white and extremely brittle, and with 10 p.c.

white, brittle, and crystalline. Aluminium containing 10 p.c. of gold is white and hard.

The malleability of aluminium is not much impaired by the addition of gold, silver, or tin, but the presence of iron, and especially of silicon, is very injurious.

With *silicon* aluminium unites in almost all proportions, either directly or by its action on silicious materials; for this reason the fusion or preparation of this metal should not be performed in any silicious crucible in presence of a flux. The presence of silicon renders aluminium brittle and much less permanent. The alloy containing 10 p.c. silicon is grey and brittle. Wöhler prepared an alloy containing 70 p.c. silicon, which still appeared metallic.

With *iron* the alloys are of especial interest. The presence of a small quantity of iron is very injurious; it renders the aluminium crystalline, and raises the melting-point. The alloy containing 5 p.c. of iron is hard and brittle; with 8 p.c. the alloy crystallises in needles, and on heating separates into a more liquid alloy containing but little iron and a skeleton very rich in that metal. Michel (Annalen, 115, 102) has prepared an alloy which crystallises in six-sided prisms, corresponding to Al_3Fe. A beautifully crystalline substance having the composition Al_4Fe is often found in the neighbourhood of the cathode of a reduction furnace.

The valuable properties imparted to iron and steel by the presence of a small quantity of aluminium have long been known; Faraday (Quarterly Journ. Roy. Inst. 1819, 290) found from 0·013 to 0·069 p.c. of aluminium in certain samples of Bombay wootz, though it has been shown by Henry and others that this metal is not always present. About the same time S. B. Rogers showed the presence of aluminium in some of the best quality of pig-iron made in South Wales, and found that a steel to which 0·8 p.c. of aluminium had been added in the form of an alloy with iron, was rendered harder and stronger and resembled the best wootz (Rogers, Metallurgy, 1858, 14). A superior steel was prepared by Sir Charles Knowles, which was stated to owe its value to the use of *kaolin* and consequent introduction of aluminium into the metal in its preparation (Mining Journal, 1859, 118).

Messrs. Cowles Bros. have exhibited a Siemens-Martin basic steel containing 0·2 p.c. aluminium, which welds with iron and shows no mark at the junction.

The addition of aluminium to iron or steel for the production of 'mitis castings' has been patented by P. Ostberg (Engineering, 1886, 360). Iron and steel, especially at temperatures far above the melting-point, absorb considerable quantities of gas, which impairs the value of the castings. The addition of 0·05 or 0·1 p.c. of aluminium to the fused iron or steel lowers the melting-point, prevents the absorption of gas, and considerably increases the fluidity. The metal can then be easily cast.

Nickel and aluminium combine with incandescence when heated together. The presence of under 3 p.c. of nickel lowers the melting-point and increases the hardness and elasticity.

Pure aluminium combines with mercury, although not readily, when the metals are heated together in an inert gas such as carbonic anhydride. The two metals combine rapidly in presence of alkalis. The amalgam may also be produced by electrolysis of mercuric nitrate, using a negative plate of aluminium dipping in mercury. When aluminium is rubbed with wash leather impregnated with mercury, combination occurs; the surface rapidly oxidises and becomes heated, with formation of concretions of alumina (Jehn and Hinze, Ber. 7, 1498).

Alloys of *bismuth* with aluminium are hard and brittle. With *antimony* and *lead* aluminium does not unite, although traces of lead are frequently present in commercial aluminium.

Sodium unites readily with aluminium. The last traces of sodium are difficult to remove, especially, it is said, when the metal has been reduced from cryolite. The alloys are easily attacked by moisture, and burn in the air, with oxidation both of the aluminium and sodium; that containing 2 p.c. of sodium decomposes water with ease. The necessity of avoiding the presence of sodium in the preparation of aluminium is therefore obvious.

Aluminium also unites with *manganese*; with *platinum* it unites easily, forming fusible alloys. With *boron* aluminium combines in varying proportions. The so-called 'adamantine' and 'graphitic' boron appear to be borides of aluminium (Hampe, Annalen, 1876, 75; and Deville and Wöhler, *ibid.* 1867, 268) (*v.* BORON).

Mallet (Chem. Soc. Trans. 1876, ii. 350) has prepared a nitride of aluminium in small crystals hard enough to scratch glass.

For further information, see J. W. Richards, Aluminium and its Alloys, London.

Aluminium oxide, *Alumina*, Al_2O_3.

Aluminium forms only one oxide, Al_2O_3, corresponding to and isomorphous with the sesquioxides of iron and chromium.

This oxide occurs native, colourless as *hyaline, corundum*; or coloured by metallic oxides, as *ruby, sapphire, oriental topaz*, &c. (*q.v.*). Very impure, dark, and usually associated with magnetite and *hæmatite*, it occurs in large boulders in many districts, and is used as a grinding and polishing material in the form of *emery* (*q.v.*). The native oxide crystallises in the rhombohedral system; in hardness it comes next to the diamond. The finely coloured specimens are used as gems. It occurs almost pure in considerable quantities in the Alleghanies in Northern Georgia.

It may be prepared by the ignition of aluminium foil in air or oxygen; the oxide so produced is fused and as hard as corundum.

Amorphous alumina may be produced by ignition of the precipitated hydrate, pure aluminium sulphate or ammonia alum; in either case alumina alone is left.

It is white and soft, but becomes hard on strong ignition. According to H. Rose (Pogg. Ann. 74, 430) the sp.gr. of the oxide after heating over a spirit-lamp is 3·725; its density may be raised to 4, just about that of corundum by heating in a porcelain furnace, but it still remains amorphous. It is remarkable that though the density of the artificially prepared alumina is nearly 4, its bulk density may be less than one-fifth of this. With a somewhat lower density the bulk density is higher, but is still such that it occupies a larger bulk than the same weight of water.

When heated by the oxyhydrogen blow-pipe, alumina melts and crystallises; the addition of chromium oxide or a chromate imparts a ruby colour to the crystals.

Fremy and Verneuil (Compt. rend. 1888, 566) have prepared artificial rubies by heating to redness a mixture of barium fluoride and alumina containing a trace of potassium dichromate. The heat requires careful management. Fine rubies are thus formed in a friable matrix which may be separated by agitation with water. By former methods the matrix was hard and difficult to remove (Fremy and Feil, Compt. rend. 1877, 1029, and 1887, 737). The crystals contain *no* barium, easily scratch the topaz, and possess the form and properties of natural rubies; their crystalline form has been determined by Descloiseaux (Compt. rend. 1888, 567). By the addition of a little cobalt oxide before the *fusion*, sapphires may be produced.

Alumina is soluble, when strongly heated, in boric acid; the latter may be driven off at a very high temperature, leaving crystalline alumina. By the addition of the proper oxide the corresponding spinels may be produced, coloured by cobalt oxide (blue), chromium oxide (red), iron oxide (black), (Ebelmen, Ann. Chim. Phys. 3, 22, 211 and 33, 34). Only two *hydroxides* of aluminium are known, viz.: Al_2O_3,H_2O and $Al_2O_3,3H_2O$. By Graham's method an aqueous solution of the hydroxide may be obtained.

When the hydroxide is freshly precipitated it dissolves readily in dilute acids, but on standing, or after filtration, solution is more difficult, and is best achieved by a mixture of 8 parts of sulphuric acid and 3 parts of water. When heated, the hydroxide loses its water, undergoing a contraction of about 30 p.c. in bulk as it passes into the form of the anhydrous oxide.

When boiled with water containing a drop of a 1 p.c. solution of alizarin, the hydroxide assumes a bright red colour, not removed by a weak solution of acetic acid.

This test easily distinguishes it from gelatinous silica. Aluminium hydroxide possesses a powerful affinity for many organic substances, and enters into association with a large number of colouring matters, precipitating them entirely as *lakes*. On this property depends the use of alum mordants (red liquor, &c.). They precipitate the hydroxide upon the fibre of the goods to be dyed, and this constitutes the *mordant* or fixing agent which retains the colour.

Sodium aluminate $Al_2O_3{\cdot}3Na_2O$ or $Al_2(NaO)_6$. This salt is now prepared on a large scale, both to be used as such and as an intermediate product in the preparation of the sulphate and other salts of aluminium.

Its formation depends upon the property possessed by alumina of acting as an acid in presence of a powerful base.

Its preparation from bauxite has been described on page 106. It may also be produced by passing a current of steam through a heated mixture of bauxite and common salt, and by strongly heating a mixture of bauxite, sodium sulphate, and carbon, but in the latter case its purification from the sodium sulphide simultaneously produced is difficult. It is also formed in the preparation of soda from *cryolite*. According to Thomsen's method, powdered cryolite is heated to redness with chalk, forming sodium aluminate and calcium fluoride:—

$$Al_2F_6{\cdot}6NaF+6CaCO_3=Al_2(NaO)_6+6CaF_2+6CO_2$$

The mass produced is lixiviated with water and fitered. From this aluminate the hydroxide is precipitated by carbon dioxide with formation of sodium carbonate:—

$$Al_2(NaO)_6+3CO_2+3H_2O=Al_2(OH)_6+3Na_2CO_3.$$

The hydroxide is usually made into aluminium sulphate by solution in sulphuric acid, or it is converted into alum.

An entirely different process has been introduced by Sauerwein. The finely powdered cryolite is boiled with milk of lime forming aluminate as before:—

$$Al_2F_6{\cdot}6NaF+6CaO=Al_2(NaO)_6+6CaF_2.$$

For the conversion of the aluminate into oxide Sauerwein applies a peculiar property possessed by that salt, which shows the readiness with which alumina loses its acid properties and again becomes basic. Sodium aluminate, when mixed in equivalent proportions with any haloid salt of aluminium, is decomposed; the sodium combines with the halogen, while the whole of the aluminium is precipitated as hydroxide. On the large scale the haloid salt used is cryolite. The finely powdered mineral is stirred into the clear liquid from the previous operation, and the alumina precipitated as hydroxide:—

$$Al_2(NaO)_6+Al_2F_6{\cdot}6NaF+6H_2O=2Al_2(OH)_6+12NaF.$$

Sodium aluminate is a white, infusible, amorphous solid, easily soluble in both cold and hot water. The concentrated solution rapidly deposits alumina, leaving in solution a basic aluminate, which on evaporation is obtained as a fusible and hygroscopic mass. The addition of any acid at once decomposes it with precipitation of alumina. This alumina is pure and free from alkali, which is never the case when alkaline precipitants have been used. It may be employed as a mordant in dyeing and calico-printing, in an acid and not, as in the case of alum, an alkaline bath. For the production of *lakes* the colouring matter is mixed with the aluminate solution and precipitated by the addition of sulphuric acid. According to Morin these lakes are richer than those obtained from alum and are produced at about one half the cost.

Potassium aluminate $Al_2O_3{\cdot}3K_2O$ or $Al_2(KO)_6$ is obtained in hard glistening crystals when alumina is fused with potash, the mass boiled in water and the solution evaporated *in vacuo*.

Aluminium chloride Al_2Cl_6. This compound was first prepared in 1824 by Oersted, by passing chlorine over a mixture of alumina and charcoal heated to redness. The method and apparatus resemble that used in the preparation of the double chloride, omitting the sodium chloride.

According to P. Curie (Chem. News, 28, 307) it may be easily prepared as follows:—Anhydrous alumina, or, less satisfactorily, clay, is strongly heated in a tube and subjected to a current of hydrochloric acid impregnated with carbon disulphide by bubbling through that liquid. Aluminium sulphide appears to be formed and at once decomposed by the hydrochloric acid, yielding aluminium chloride and sulphuretted hydrogen. The condensed chloride

may be freed from sulphur by distillation with iron filings.

A solution of the chloride may be obtained by dissolving the hydroxide in hydrochloric acid.

The pure anhydrous chloride is a white, waxy, crystalline solid; in presence of a trace of iron it becomes yellowish. On heating, it volatilises without fusion. If large pieces be quickly heated they fuse and boil at 180° to 185° (Liebig). It is very hygroscopic, and evolves hydrochloric acid on exposure to the air; is easily soluble in water; soluble in alcohol and ether. When deposited from a solution in hydrochloric acid, it forms crystals of the formula $Al_2Cl_6,12H_2O$.

It absorbs ammonia and combines with many metallic chlorides, forming double chlorides, the most important being that with sodium. Aluminium chloride has been recommended by Filsinger (Chem. Zentr. 10, 1270) for the preservation of wood, and by Saget (Chem. News. 45, 113) and others (J. Soc. Chem. Ind. 1882, 185 and 230) for the production of a discharge on indigo blue. An impure chloride containing calcium and sodium salts is stated to be largely used as a disinfectant under the name 'Chloralum.'

Double chloride of aluminium and sodium $Al_2Cl_6,2NaCl$. This compound may be produced by fusing together the proper proportions of aluminium and sodium chlorides. It is a colourless crystalline solid, melting at 185° (Deville) and volatilising at a red heat. It is slightly hygroscopic, but much less so than aluminium chloride; it is also more stable and more satisfactory in use than that substance, and gives up nearly the whole of its aluminium when reduced by sodium.

Aluminium bromide Al_2Br_6 is most readily prepared by the action of bromine on metallic aluminium. The action is violent, and the metal should only be added gradually. A lump of aluminium weighing twenty grams becomes strongly heated and even fused on being placed in cold bromine (Mallet, Phil. Trans. 171, 1018).

It may also be prepared by the action of bromine on a strongly heated mixture of alumina and carbon, and, in solution, by dissolving the hydroxide in hydrobromic acid. It crystallises in colourless shining laminæ, which melt at 93° (Deville and Troost) and boil at 263·3° (at 747 mm.) (Mallet).

Like the chloride, it forms a double bromide, $Al_2Br_6,2KBr$.

Aluminium iodide Al_2I_6 may be prepared by heating aluminium with iodine in a closed tube. It melts at about 185° (Weber) and boils at 350° (Deville and Troost); its vapour is combustible. It dissolves in water, alcohol, and carbon disulphide.

Aluminium fluoride Al_2F_6, may be prepared by the action of gaseous silicon fluoride, or of hydrofluoric acid upon aluminium. It forms transparent rhombohedra, volatile at a red heat, insoluble in water and unacted upon by acids. In solution in hydrofluoric acid, it appears to form the compound $Al_2F_6{\cdot}6HF$, the acid corresponding to the double fluoride of aluminium and sodium.

Cryolite $Al_2F_6{\cdot}6NaF$. This important compound may be prepared artificially, and attempts have been made to produce it as a substitute for the natural cryolite, it being claimed that the artificial cryolite possesses the advantage of being lighter and melting at a lower temperature (J. Soc. Chem. Ind. 1890, 945). Natural cryolite occurs in quantity only in one locality, in a large vein in the gneiss at Ivigtut in Greenland. Greenland cryolite has the following composition: Al 13·2, Na 32·7, F 54·2, and small quantities of manganese. The melting-point of mixtures of cryolite and alumina is said to be—

Cryolite	1000°
With 3 p.c. Al_2O_3 . .	974°
„ 6 p.c. „ . .	960°
„ 10 p.c. „ . .	980°
„ 15 p.c. „ . .	994°
„ 20 p.c. „ . .	1015°

(Chem. Soc. Abst. 1907, 469).

It is a semi-transparent, white, crystalline, brittle solid, which melts at the edges in a candle flame. Its hardness is 2·5 to 3; its sp.gr. 2·95. When impure it is frequently yellowish-red or even black (*v.* CRYOLITE).

Cryolite is used as a flux in the manufacture of aluminium; formerly for making salts of sodium and aluminium; and for the manufacture of an opaque, porcelain-like glass. It is also used for enamelling pans and as a glaze for pots as replacing lead glaze. (*See* further, Benzon, (Hoffmann's Ber. Entw. Chem. Ind. [1] 660).)

Aluminium sulphide Al_2S_3, may be prepared by strongly heating a mixture of aluminium and sulphur, or by heating alumina to bright redness in the vapour of carbon disulphide. It forms a yellow, glassy mass, which fuses with difficulty, and burns in air with production of alumina and sulphur dioxide. It is at once decomposed by water. Houdard (Compt. rend. 1907, 801) found that by heating aluminium turnings and sulphides of manganese iron and chromium in a carbon boat, sulphides related to the spinels are formed, of which he prepared

$$MnS,Al_2S_3,\ FeS,Al_2S_3,\ CrS,Al_2S_3.$$

Aluminium carbide Al_4C_3 may be obtained by the action of carbon or the oxides of carbon on alumina at very high temperatures, and often occurs in small quantity in the neighbourhood of the cathode of aluminium reduction furnaces in the form of a yellow powder; it is formed when a mixture of alumina and carbon is submitted to a current of 300 amperes at 35 volts. It possesses the remarkable property of being stable at high temperatures, and yet undergoing decomposition at a dull red heat. It reacts, though somewhat slowly, with water or dilute acids with the production of methane. The formation of carbide and ultimately its decomposition has been proposed as a means of preparing alumina from clay or other crude materials. Pring (Chem. Soc. Trans. 1905, 1530) found that up to 1400°C. the carbide acts as a reducing agent on metallic oxides,

$$Al_4C_3+12MO=2Al_2O_3+3CO_2+12M,$$

but at higher temperatures alloys of aluminium and the metal are produced, only carbon being oxidised,

$$Al_4C_3+3CuO=Al_4Cu_3+3CO,$$

owing to the fact that alumina can be reduced by carbon at very high temperatures; at lower temperatures the aluminium is oxidised by carbonic oxide as observed by Moissan,

$$6Al+3CO=Al_4C_3+Al_2O_3,$$

the reaction being reversed at the higher temperatures.

Aluminium sulphate $Al_2O_3(SO_3)_3,18H_2O$ or $Al_2(SO_4)_3,18H_2O$. Aluminium sulphate occurs naturally in considerable quantities. As the hydrated salt of the above composition, it forms the chief constituent of the mineral *alunogen, halotrichite, feather alum,* or *hair salt,* which is found in volcanic districts, at Bilin in Bohemia, Copiapo in Chili, &c. It also occurs in pyritic shale. A sample of feather alum from Friesdorf, Bonn, was found by Rose to contain Al_2O_3 14·9 p.c., SO_3 37·4 p.c., FeO 2·5 p.c., H_2O 45·2 p.c., with traces of K, Na, Mg, and SiO_2.

Aluminite or websterite, a hydrated basic salt of the composition $Al_2O_3SO_3,9H_2O$, has been found at Auteuil, Halle, Muhlhausen, &c.

In combination with potassium sulphate, the basic salt occurs also in *alunite, alumstone,* or *alum rock* $K_2SO_4,3Al_2O_3(SO_3),6H_2O$, a mineral which is found in large quantities at La Tolfa near Civita Vecchia, in Hungary, at Puy-de-Sancy and Madriat in Auvergne, and in many other localities. It usually occurs in fibrous compact masses in trachyte, of colour varying from white to red or brown, being produced by the action of sulphurous gases upon trachytic rocks rich in felspar.

The alunite from La Tolfa contains from 35 p.c. to 17·5 p.c. alumina; the average composition of the mineral is Al_2O_3 27·6 p.c., SO_3 29·74 p.c., K_2O 7·55 p.c., Fe_2O_3 1·2 p.c., SiO_2 22·7 p.c., H_2O 11·2 p.c.

Aluminium sulphate may be produced by dissolving either the hydrated oxide or the silicate in sulphuric acid. Of the raw materials available for its manufacture, the two which are of the greatest importance at the present time are china clay (kaolin) and bauxite. China clay is a very pure variety of clay, resulting from the natural decomposition of felspar, and approximating in composition to the formula $Al_2O_3,2SiO_2,2H_2O$. It is of comparatively rare occurrence, being found chiefly in Devon and Cornwall in England; at St. Yrieix near Limoges, and in the departments of Allier, Puy-de-Dome, and Brittany, in France; at Seilitz in Saxony; and at Nassau in Bavaria.

Bauxite is an impure aluminium hydroxide $Al_2O_3,2H_2O$, containing widely varying quantities of silica and ferric oxide. It is found in Ireland, in the south of France, and in Austria, Calabria, Senegal, &c. (*v.* BAUXITE).

The composition of typical commercial grades of the two minerals is given in the following table, the analyses having been made on material dried at 100°:—

Source	China clay		Bauxite	
	St. Stephen's	St. Austell	Antrim	France
Al_2O_3	40·15	41·10	41·08	64·18
Fe_2O_3	0·35	0·20	3·21	3·47
SiO_2	45·00	46·20	33·17	18·96
TiO_2	—	—		
K_2O+Na_2O	0·80	trace	—	—
H_2O (comb.)	13·70	12·50	22·54	13·39
Total	100·00	100·00	100·00	100·00

Production of aluminium sulphate from china clay.—At the present time the manufacture of aluminium sulphate from china clay is carried out on an extensive scale by a process based upon the original patent of Pochin (Pat. 1855, 14656). The clay, containing about 40 p.c. alumina, is obtained from Cornwall, and is selected as free as possible from grit and oxide of iron. It is reduced by milling and sifting to the finest possible state of division, and after a preliminary drying by exposure to a warm atmosphere, is calcined at a dull-red heat in a reverberatory furnace. The furnace is provided with three working doors, the material being introduced by the door which is most remote from the firegrate, and gradually raked forward until it reaches the hottest part of the hearth. During the calcination the clay suffers a loss in weight amounting to from 20 to 25 p.c., due to the expulsion of the whole of the moisture present (10 to 15 p.c.) and of the greater part of the water of hydration.

The calcined clay, which still contains about 3 p.c. of water, is transferred by means of iron tubs to a lead-lined wooden vat containing the requisite quantity of sulphuric acid, heated to a temperature of 85°, and having a strength at this temperature of 96°Tw. A vigorous reaction immediately takes place, and after the lapse of 15 minutes, during which period the contents of the vat are kept well agitated, the product is run into lead-lined wooden waggons (with removable sides), in which the reaction continues for a considerable time and the pasty mass gradually solidifies. Finally the solid block is brought under a heavy mechanical knife, and by a combined cutting and crushing action is reduced to the state of a coarse powder.

The product, which is brought on the market under the name of 'alum cake,' contains the whole of the silica, iron, and other impurities present in the clay, its average composition being: Al_2O_3 (soluble) 12·25 to 13·0 p.c., Fe_2O_3 0·12 to 0·22 p.c.; combined SO_3 29·5 to 31·8 p.c., free SO_3 0·4 to 1·0 p.c.; insoluble matter 20·0 to 26·5 p.c.

About 60 p.c. of the alumina present in the china clay is converted into sulphate.

The commercial 'white sulphate of alumina' is prepared from alum cake in the following manner: The coarsely crushed alum cake is lixiviated with water (or with weak liquors from previous extractions) in lead-lined vats heated by live steam; after settling, the clear solution is decanted by means of a hinged pipe, and run into lead-lined evaporators, heated by steam coils, where it is concentrated to a strength of 112°Tw. at the boiling-point (about 115°). The syrupy liquid is then run into a series of shallow tiled troughs, where it solidifies on cooling. Before solidification occurs, a number of leaden partitions are inserted in the troughs, and the product is thus obtained in the form of rectangular blocks of uniform size (24″×9″×6″). 'White sulphate of alumina,' prepared by the above process, contains on an average about 14 p.c. of alumina and 0·25 p.c. of ferric oxide, and is practically free from insoluble matter. Another grade of the material is prepared containing 17·5 p.c. alumina.

Preparation of aluminium sulphate from bauxite.—The substitution of bauxite for china

clay in the manufacture of aluminium sulphate was proposed by Lechatelier in 1858, and its treatment forms the subject-matter of numerous patents. Bauxite has the advantage over china clay that it is more readily solubie in acid, and needs no preliminary calcination, the chief drawback to its use being the presence of a comparatively large amount of iron.

The treatment of bauxite for the preparation of 'alumino-ferric cake,' as patented by Messrs. P. and F. M. Spence (1875), is as follows:—The mineral is digested with dilute sulphuric acid with the aid of steam until the acid is neutralised; the insoluble matter allowed to subside, and the solution evaporated to 100°Tw. and run into shallow-partitioned lead coolers. It there solidifies, and is removed in blocks 18 or 20 inches square, each weighing about 1 cwt. It is yellowish-green in colour, contains much alumina, and a small proportion of iron and free acid. It is used in the preparation of all but the finest papers, in the precipitation of sewage and refuse liquids, and in the clarification and decolourisation of water supplies. The following analysis shows its general composition: Al_2O_3 14·26 p.c. (corresponding to $Al_2O_3 3SO_3$ 47·61 p.c.), Fe_2O_3 0·28 p.c., FeO 0·32 p.c. SO_3 (combined) 35·36 p.c., SO_3 (free) 0·45 p.c. Insoluble 0·06 p.c.

The commercial sulphate of alumina which is sold under the names of 'concentrated alum' and 'alferite,' resembles alumino-ferric in composition, and is prepared by a similar process. The following details concerning its manufacture will serve to exemplify modern practice.

As raw material, it is usual to employ a mixture of Irish and French bauxites, reduced by means of disintegrators to the state of a coarse powder. The powdered mineral is conveyed by means of an elevator to a lead-lined vat containing sulphuric acid, heated to its boiling-point (about 112°), and having a strength, at this temperature, of 96°Tw. The mixture of acid and bauxite is boiled vigorously for 6 hours, after which it is diluted with weak liquors to 70°Tw. (measured at the boiling-point) and allowed to settle. The clear liquor is decanted and evaporated in lead-lined vessels until its density reaches 112°Tw. (boiling). It is then run into partitioned coolers where it solidifies, forming blocks or slabs, containing on an average 13·8 p.c. alumina, 0·7 p.c. ferric oxide, and 0·1 p.c. insoluble matter.

If French bauxite be used alone in the above process, great difficulty is experienced in the clarification of the liquor; with a mixture of Irish and French bauxites, however, rapid settling occurs, and a perfectly clear liquor is readily obtained. It is of importance also, in this connection, that the liquor should retain a small amount of free acid, as the fully neutralised solution settles very slowly.

Sulphate of alumina prepared by any of the above processes always contains appreciable quantities of iron, and the removal of this impurity is a problem of considerable importance, and one which has received the attention of many chemists. Numerous processes have been devised for the purpose, but it is doubtful if any of these is satisfactory in works' practice.

Newlands (Eng. Pat. 1880, 5287) evaporates a crude solution of the sulphate to a density of 67°Tw. (at 200°F.) and cools for twenty-four hours in leaden tanks.

About 60 p.c. of the sulphate thus crystallises out. The liquid is drained off, and the residue pumped or forced into lead-lined filter presses, the plates of which are covered with thick felt, and separated by metal rings. Here it is subjected to a pressure of about 200 lbs. to the square inch. The hard cake so produced contains about 67 p.c. of the total aluminium sulphate, and 0·05 to 0·1 p.c. of iron. The mother liquor, evaporated and similarly treated, yields a second and third crop of crystals containing increasing quantities of iron.

Chadwick and Kynaston have patented a method for the removal of iron from bauxite before converting the latter into aluminium sulphate. The powdered mineral is mixed to a thick cream with water, and treated with 5 to 10 p.c. of oxalic acid and sufficient hydrochloric acid to prevent the formation of insoluble oxalates. After seven to ten days the mass is washed, and a large proportion of the iron (together with some of the alumina) is thus removed as oxalate.

Condy, in 1877, proposed the reduction of the iron by reducing agents, or its conversion into sulphide by sulphuretted hydrogen, and the removal of the metal or sulphide by dilute acid. The proportion of iron may thus be reduced to one-third.

Weismann suggested the precipitation of the iron from aluminium sulphate liquors by means of potassium ferrocyanide. The method is by no means satisfactory, as the precipitate contains much alumina and subsides very slowly.

Kynaston precipitates the bulk of the iron as ferric arsenite, removing the last portions with calcium ferrocyanide, followed by the addition of copper or zinc sulphate.

According to Fahlberg and Semper (Eng. Pat. 1881, 5579), both ferrous and ferric salts may be precipitated from aluminium sulphate by agitation in the cold for about thirty minutes with lead peroxide, ferrous salts being first oxidised and then precipitated. No lead passes into solution unless chlorides be present. The composition of the precipitate is not known, but the peroxide may be regenerated by digestion in cold nitric acid. P. and F. M. Spence (Eng. Pat. 1882, 3835) use manganese dioxide for the same purpose. In presence of reducing agents such as ferrous salts, &c., manganese passes into solution, and requires to be reprecipitated by addition of chlorine or a hypochlorite.

The use of metantimonic acid and metastannic acid (Hood and Salamon) has also been proposed for the precipitation of iron. The iron is first oxidised by the addition of bleaching powder, and the liquid is neutralised with chalk and agitated with the precipitant. Both substances may be regenerated by digesting the precipitate with sulphuric acid.

(For further information regarding these processes, *see* Beveridge (J. Soc. Chem. Ind. 1886, 16–22); B. E. R. Newlands (*ibid.* 1882, 124); Kynaston (Chem. News, 40, 191 and 202).)

The above-mentioned processes for the

purification of aluminium sulphate from iron possess little or no commercial significance at the present time. 'Pure aluminium sulphate' is prepared directly from *pure* alumina, which is obtained from bauxite by the 'alkali fusion' process. The bauxite, reduced to a fine powder, is mixed with soda ash in such proportions that for every molecule of Al_2O_3 (including Fe_2O_3) present there are 1 to 1·2 molecules of Na_2O. The mixture is strongly heated in a reverberatory furnace, with frequent stirring, for a period of five hours. Carbon dioxide is evolved and the alumina and ferric oxide are converted into sodium aluminate and sodium ferrite respectively. The mass is lixiviated by successive extractions, first with weak liquor from previous batches, and finally with pure water. The sodium aluminate dissolves as such, whilst the sodium ferrite is decomposed, forming insoluble ferric oxide which remains in the exhausted residue, and caustic soda which passes into solution. The clear liquor is run into a boiler and saturated with carbon dioxide produced by the combustion of coke or by the decomposition of limestone. During the passage of the gas the contents of the boiler are heated to 70° and kept thoroughly stirred by means of an agitator. When the precipitation of the alumina is complete, the liquid is allowed to settle and the clear liquor decanted and concentrated for the recovery of the dissolved sodium carbonate, whilst the alumina is drained in a hydro-extractor.

A cheaper process for obtaining the alumina from the sodium aluminate has been devised by Bayer (as described, p. 106).

The alumina prepared by either of the above processes yields by treatment with sulphuric acid, a very pure quality of aluminium sulphate. Two grades of the latter are commonly prepared for the English market—the one, sold in the form of slabs or blocks, contains 14·0 p.c. of alumina and 0·0025 p.c. of ferric oxide, the other, sold in powder, contains 18·0 p.c. of alumina and 0·0040 p.c. of ferric oxide.

Aluminium sulphate crystallises with difficulty in thin, six-sided nacreous plates, containing 18 molecules of water and having a density of 1·6913 at 17° (Dewar). The following table of solubilities is given by Poggiale (Ann. Chim. Phys. [3] 8, 467) for the crystalline and anhydrous salts :—

Temp. °C.	Solubility in 100 parts of water	
	$Al_2(SO_4)_3$	$Al_2(SO_4)_3,18H_2O$
0	31·3	86·8
10	33·5	95·8
20	36·1	107·3
30	40·4	127·6
40	45·7	167·6
50	52·1	201·4
60	59·1	262·6
70	66·2	348·2
80	73·1	467·3
90	80·8	678·8
100	89·1	1132·0

The addition of alcohol, in which aluminium sulphate is almost insoluble, to aqueous solutions of aluminium sulphate, facilitates the crystallisation of the salt (Persoz).

Karl Reuss (Ber. 17, 2888) gives the density of solutions of pure anhydrous aluminium sulphate as follows :—

Percentage	Density at 15°C.	Percentage	Density at 15°C.
1	1·017	14	1·1467
2	1·027	15	1·1574
3	1·037	16	1·1668
4	1·047	17	1·1770
5	1·0569	18	1·1876
6	1·0670	19	1·1971
7	1·0768	20	1·2074
8	1·0870	21	1·2168
9	1·0968	22	1·2274
10	1·1071	23	1·2375
11	1.1171	24	1·2473
12	1·1270	25	1·2572
13	1·1369		

Percentage	Density at 25°C.	Density at 35°C.	Density at 45°C.
5	1·0503	1·0450	1·0356
10	1·1022	1·0960	1·0850
15	1·1522	1·1460	1·1346
20	1·2004	1·1920	1·1801
25	1·2483	1·2407	1·2295

When heated, aluminium sulphate melts in its water of crystallisation, swells up, and gradually forms a white porous mass of the anhydrous sulphate, which only dissolves slowly in water. At a red heat oxides of sulphur are expelled and a residue of pure alumina remains.

Aluminium sulphate combines readily with the sulphates of the alkali metals, forming crystalline double sulphates, known as alums, which are, as a rule, considerably less soluble than aluminium sulphate itself. According to Reuss (Ber. 17, 2888), the addition of 1 p.c. of potassium sulphate to a solution containing 7 p.c. or upwards of aluminium sulphate, at once produces a crystalline precipitate of alum.

The general industrial uses of aluminium sulphate are the same as those of ordinary alum. It is largely used in paper-making and in the preparation of red liquor as a mordant. The coarser preparations are employed for the precipitation of sewage.

For the detection of free acid in aluminium sulphate, Miller (Ber. 1883, 1992) recommends the use of methyl orange, which yields an orange-coloured solution with the pure sulphate, but is reddened by free acid. A dilute solution of Congo red becomes blue in presence of free acid, but is not affected by the pure salt.

For the estimation of the free acid, a weighed quantity (20 to 50 grams) of the sample is dissolved in 40 to 100 c.c. of water, the solution heated to boiling, and titrated with normal caustic soda until a drop of the liquid, taken out with a glass rod, fails to yield a blue colour when mixed with six drops of Congo red solution (prepared by dissolving 0·067 gram. of Congo

red in 100 c.c. of boiling water and diluting to a litre).

T. J. I. Craig (J. Soc. Chem. Ind. 1911, 184) proposes to determine the free acid in aluminium sulphate by treating the latter with excess of neutral potassium fluoride, whereby the double salt $AlF_3 \cdot 3KF$ is formed together with potassium sulphate. As these products, are neutral to phenolphthaleïn, the free acid present may be directly titrated with a standard solution of potassium hydroxide.

Iron, in the ferrous condition, is estimated by titration with decinormal potassium permanganate, and total iron by means of standard titanous or stannous chloride solution. If the quantity of iron present be very small, it is determined colorimetrically (*v.* ALUMS).

Several basic aluminium sulphates have been prepared. The compound $Al_2O_3,2SO_3,12H_2O$ is obtained by heating a solution of aluminium sulphate with zinc, or by dissolving in it the calculated quantity of aluminium hydrate. Spence and Sons, Limited (D. R. P. 1903, 167419), prepare a basic sulphate of similar composition by heating sulphuric acid under pressure with 15 to 30 p.c. more alumina than is required for the formation of the normal salt. The solution is then treated with sufficient chalk or lime to raise the basicity by 20 to 28 p.c. The strongly basic solution is rapidly filtered and concentrated *in vacuô* until its density reaches 1·45. On cooling with agitation, a magma of crystals is formed and is separated by suitable means from the mother liquor which contains normal aluminium sulphate (compare also Eng. Pat. 1902, 25683, and Fr. Pat. 1903, 331836).

ALUMINIUM BRONZE *v.* ALUMINIUM.

ALUMS. This generic name is given to an important group of double salts of the general type $R_2SO_4,R'_2O_3(SO_3)_3,24H_2O$, where R is a monovalent metal or basic radicle such as potassium, sodium, ammonium, &c., and R'_2O_3 is a sesquioxide such as that of aluminium, iron, chromium, or manganese. They are all soluble in water, and crystallise therefrom with twenty-four molecules of water, in forms belonging to the regular system, usually octahedra or cubes.

The alums which contain the sesquioxide of alumina will alone be considered here, and of these the most important are the potassium, sodium, and ammonium compounds.

'Selenic alums' have been prepared, in which sulphuric acid is replaced by selenic acid.

Potassium alum, *Potash alum*

$$K_2SO_4,Al_2O_3(SO_3)_3,24H_2O.$$

This salt is found in nature as *kalinite*, in the form of fibrous crystals or as an efflorescence on aluminous minerals, and occasionally also in octahedra, at Whitby, Campsie, &c. In the Solfatara near Naples, and the islands of Volcano and Milo, it occurs in larger quantities, being formed by the action of volcanic gases upon felspathic trachyte.

Of greater importance is the mineral *alunite* or *alumstone*, which is a double salt of potassium sulphate and basic aluminium sulphate, having the composition $K_2SO_4,Al_2(SO_4)_3,2Al_2(OH)_6$; it is found at La Tolfa near Civita Vecchia; at Montioni in the Duchy of Piombino; at Mursaly, Munkact, and Tokay in Hungary; in the islands of Milo, Argentino, and Nipoglio (Grecian Archipelago); at Puy-de-Sancy and Madriat (Auvergne); at Samsoun in Asia Minor; and in Australia. An 'alum mountain,' composed of this mineral, is reported to exist in China, and is stated to be nearly 1900 feet high and to have a circumference at its base of about ten miles (U. S. Cons. Report, 1903).

The manufacture of alum is of great antiquity. In the time of Pliny alum was in use as a mordant for the production of bright colours, and was even tested by means of the *tannin* in pomegranate juice to ascertain its purity. It was prepared in the thirteenth century at Smyrna from alum rock, and since the fifteenth century has been largely produced at La Tolfa from the same substance.

Its preparation from pyritic shale has long been known, together with the fact that the presence of an alkali was necessary to induce crystallisation, but, until proved in 1797 by Chaptal and Vauquelin, the essential presence of alkali in the crystals was not recognised.

Very pure alum is prepared in small quantities at Solfatara. The natural alum found there is digested with water in large wooden vats under cover, and maintained at about 40° by the natural heat of the soil. The solution is decanted and crystallised. A second crystallisation produces extremely pure alum.

Production of alum from alunite.—The preparation of alum from alunite is an industry which dates from very early times. Of Oriental origin, it appears to have been introduced into Europe in the thirteenth century, and during the fifteenth century several alum works were established. Amongst these may be mentioned the celebrated works at La Tolfa near Civita Vecchia, a district in which alum manufacture still ranks as an important industry.

The outline of the La Tolfa process given below is of historical interest. The mineral, broken into lumps of moderate size, is calcined at a low red heat, either in heaps or in kilns. The operation requires to be carefully performed, and is stopped as soon as the mineral begins to evolve acid fumes. The calcination occupies about six hours and results in a loss in weight amounting to about 33 p.c., chiefly due to the expulsion of water; at the same time the basic sulphate is decomposed, yielding alum and insoluble alumina. The roasted mass is transferred to brickwork bins and exposed to the air for several months, during which time it is occasionally moistened. The resulting sludge is lixiviated with water at 70°, and the clear decanted liquor concentrated. The crystals of alum which separate on cooling are cubic and have a reddish tinge owing to the presence of suspended ferric oxide; this may be removed by recrystallisation. The amount of soluble iron present is stated to be less than 0·005 p.c. The product, known as Roman alum, was in former times highly valued on account of its great purity.

In the modern process, employed on the Continent, the alunite is calcined at a higher temperature and the product treated with sulphuric acid, whereby aluminium sulphate is formed from the excess of alumina, and passes into solution together with the alum. The

latter is either crystallised out, and the more soluble aluminium sulphate recovered as such from the mother liquors, or sufficient potassium sulphate is added to convert the whole of the aluminium sulphate into alum.

According to C. Schwartz (Ber. 17, 2887), the best temperature for the roasting is 500°, and the acid used should have a density between 1·297 and 1·530. L. Geschwind (Manufacture of Alum and the Sulphates of Alumina and Iron, 1901), however, states that in France a temperature of about 1000° is employed.

Formerly, the greater portion of the alum manufactured in England was prepared from alum shale (alum ore), alum schist, and similar minerals, which occur in large quantities at Whitby in Yorkshire, Hurlet and Campsie in Scotland, in Sweden, Norway, Belgium, and in several parts of Thuringia, Westphalia, &c. These minerals are mixtures of aluminium silicate, iron pyrites, and bituminous substances; the iron pyrites is principally present in the aluminous schists as a fine black powder, disseminated throughout the mass, and not distinguishable to the eye. The rapid oxidation of these minerals under atmospheric influences or heat is due to this state of fine division.

Aluminous earths are dark brown, friable, porous masses without structure, and contain less silica than the schists. They usually occur in layers with lignite.

Production of alum from aluminous shale.—The more earthy shales are porous, and if piled in heaps in the open air and occasionally moistened undergo spontaneous oxidation, with the formation of sulphates of iron and aluminium. Usually they require roasting, and when not sufficiently bituminous for combustion, are first mixed with fuel.

The coarsely broken shale is built up with alternate layers of coal into heaps, which are ignited. As the mass burns, fresh quantities of the mineral are added, until a sufficient mass of material has been accumulated. By pumping water over the surface at intervals the temperature is regulated to a degree suitable for rendering the decomposition as complete as possible. Too high a temperature is to be avoided, as it results in the loss of sulphur dioxide and the formation of a slag. During the combustion of the shale the pyrites is decomposed, giving up a portion of its sulphur, which is converted by burning into sulphur dioxide, and this in conjunction with atmospheric oxygen attacks the clay, forming aluminium sulphate. The calcined mass is allowed to remain exposed to the air for a considerable period, during which a further absorption of oxygen takes place, resulting in the conversion of the lower sulphide of iron into ferrous sulphate and ferric oxide.

Lixiviation.—This operation is carried out in large lead-lined boxes with perforated bottoms, the filtering bed being formed of timber topped with brushwood. A layer of the roasted mineral about 13 inches deep, is introduced and its extraction is effected, first with the mother liquor from the alum crystallising pans, and later with pure water, the liquid in each case being left overnight in contact with the material.

The exhausted mineral still contains a considerable amount of alumina and sulphuric acid. The liquors, which have a density of 1·09 to 1·15, are run into settling tanks and allowed to deposit calcium sulphate, ferric oxide, and other suspended impurities, and are then removed for concentration. The method adopted for this purpose varies according to the nature of the mineral under treatment. In the case of shales from Hurlet and Campsie the concentration is effected by surface evaporation in a reverberatory furnace.

The bed is of stone, coated with well-rammed clay, 4 or 6 feet wide, 2 or 3 feet deep, 30 or 40 feet long. It is filled to the brim with strong liquor, and the flame and hot air from the fire carried over it. As evaporation proceeds, more liquor is added until the proper concentration is reached. It is then run into leaden pans, concentrated to about 1·4 sp.gr. and conveyed to a precipitating cistern containing the requisite quantity of dry potassium chloride; the liquid is well agitated and the chloride soon dissolves. In about 5 days the liquor is drained from the large crystals, which are washed and recrystallised.

The Whitby shales differ from those at Hurlet, in that they contain a considerable quantity of magnesia which passes into the extract in the form of magnesium sulphate. In this case surface evaporation is not satisfactory on account of the formation of a crust of this salt which retards evaporation. The evaporation of the liquor is carried out, therefore, in leaden vessels, until a sp.gr. of 1·125 to 1·137 is reached, after which the solution is allowed to stand until clear. The concentration is continued up to sp.gr. 1·25, at which stage a sample of the liquor is withdrawn and the percentage content of aluminium sulphate determined. After further evaporation to a density of 1·4 to 1·5, the hot liquor is run into a precipitating tank and mixed with a saturated solution of the calculated quantity of potassium chloride or sulphate, the whole being kept in constant agitation to induce the formation of small crystals (alum meal).

When much ferric sulphate is present in the solution, the addition of potassium sulphate would produce iron alum, isomorphous with ordinary alum, which would crystallise out and contaminate the product. The use of potassium chloride prevents this, by producing the easily soluble ferric chloride, while ferrous salts are converted into the equally soluble ferrous chloride, an equivalent amount of potassium sulphate being formed at the same time. Chloride of potassium is generally employed in preference to the sulphate, whenever sufficient iron sulphate is present to supply the requisite amount of sulphuric acid for the formation of alum; its greater solubility is also in its favour. Too much chloride should be carefully avoided, for after the iron sulphates have been decomposed, the aluminium sulphate is itself attacked, with the production of the very soluble chloride, which is lost.

The *alum meal*, consisting of small brownish crystals, is drained and washed twice with cold water. The adhering mother liquor, containing much iron, is thus removed, and the meal is left nearly pure. The final purification is effected by dissolving in a minimum quantity of boiling water and allowing the solution to stand for about eight days in casks furnished with movable

staves. At the end of this period the staves are removed, the block of crystals is pierced, the mother liquor drained off and employed for dissolving fresh quantities of meal.

The mother liquor from the alum meal has a sp.gr. of about 1·4; it contains sulphate or chloride of iron, magnesium sulphate, &c., and will yield more alum on evaporation. In a final evaporation it yields ferrous sulphate in fine green crystals. When iron is present in large quantity, the liquors are evaporated and the ferrous sulphate crystallised out before the addition of the potassium salt. In this case the iron salt is less pure and less soluble, but the alum subsequently produced contains less iron.

Formerly, potassium alum was alone produced. In 1845, however, the potassium sulphate was replaced by the ammonium sulphate produced from the then waste liquors from gas works, yielding ammonium alum. This great improvement was introduced by the late Peter Spence; his method was soon generally adopted both in England and on the Continent.

Another great advance was made by Spence in 1845 in the manufacture, by the treatment of the refuse shale underlying the coal-seams of South Lancashire. This shale contains from 5 to 10 p.c. of carbonaceous matter. It is piled upon rows of loosely placed bricks (to allow a free passage to the air) in heaps 4 or 5 feet high and 20 feet long. The combustion is started with a little fuel, but the shale contains sufficient combustible matter to continue burning. The calcination is performed slowly at a heat below redness. In about 10 days the roasting is completed, and the material has become soft, porous, and light red, whilst the alumina contained in it has become anhydrous and soluble in sulphuric acid. Too high a temperature, however, partially vitrifies it, in which case it is only slowly attacked by acid. Charges of 20 tons are placed in large covered pans 40 feet long, 10 feet wide, and 3 feet deep, lined with lead, and are digested for about 48 hours with sulphuric acid (of sp.gr. 1·35) at 110°, the temperature being maintained by fires beneath the boilers. Formerly ammonia was forced into the liquid from a boiler containing gas liquor; ammonium sulphate was thus produced, with considerable rise of temperature, and combined with the aluminium sulphate forming ammonium alum. The solution of alum so produced is run into cisterns 29 feet by 17 feet, and 1¼ feet deep, in which it is kept in constant agitation. In about 14 hours the small crystals so formed are drained, washed with some mother liquor from 'block alum,' and dissolved by a process known as 'rocking' for the production of pure block alum. For this purpose they are introduced into a hopper, at the bottom of which they encounter a current of steam at a pressure of 20 lbs. per sq. inch, both steam and crystals being supplied in such proportions that all the crystals are dissolved, while no steam is wasted. In this manner 4 tons of crystals may be dissolved in 30 or 40 minutes. The solution is run into a leaden tank, and, after a time, treated with a small quantity of size, which precipitates a quantity of insoluble matter. The clear liquid is next run into tubs about 6 feet high and 6 feet wide, tapering upwards, with movable lead-lined staves. After some days the staves are removed and a hole is bored in the mass of crystals for the removal of the liquor. Each block weighs about 3 tons, while the mother liquor contains about 1 ton.

To produce 1 ton of ammonium alum by this method on an average about 15 cwts. of the shale is required.

A great advantage of this process is the speed with which the crude material is converted into marketable alum. By the old process twelve months was required for this conversion, whilst by Spence's process the whole operation is performed in one month. For this process Spence was awarded the medal for alum manufacture at the Exhibition of 1862, at which date he manufactured 150 tons of alum weekly, over one-half the total production of England (*v.* Hofmann's Report on Chemical Processes at the Exhibition of 1862, p. 62, and J. Carter Bell, Chem. News, 12, 221).

Alum is also produced by the addition of potassium sulphate to aluminium sulphate, prepared by any of the processes already described. It is prepared in great purity from the sulphate produced from cryolite; 1 ton of cryolite produces 3 tons of alum (*v. Sodium aluminate*).

Many other processes have been proposed and used for the preparation of alum.

Spence, in 1870 (Eng. Pat. 1676), patented a method of preparing alum from mineral phosphates, especially that from Redonda near Antigua, which contains 26·1 p.c. of alumina as phosphate with ferric oxide and silica. It is calcined at a red heat to render it porous, powdered, and digested with sulphuric acid of sp.gr. 1·6 in quantity proportional to the amount of alumina, in lead-lined vessels, heated by steam. The liquid is concentrated to a density of 1·45, and treated with the requisite amount of potassium sulphate to convert the whole of the alumina into alum. Phosphate containing 20 p.c. of alumina yields about 1½ times its weight of alum, from which, however, the last traces of phosphoric acid are removed with difficulty. The phosphoric acid in the mother liquors is valuable as a manure.

Methods have frequently been proposed for the preparation of alum from felspar. Ordinary felspar contains both potassium and aluminium combined with silica in larger proportions than are contained in alum; the problem to be solved is the substitution of sulphuric acid for silica. A method adopted by Turner, said to have been originated by Sprengel, consisted in the ignition of a mixture of one part of the powdered mineral with one part of potassium bisulphate until fused; one part of sodium carbonate was then added, and the whole again fused. The mass was boiled with water and the insoluble double silicate remaining was decomposed by hot sulphuric acid of sp.gr. 1·20, and the alum crystallised out. On account of the high temperature required, this process was not successful.

At the present time the bulk of the alum manufactured in England is prepared either from shale or from the aluminium sulphate derived from bauxite or china clay.

For the more delicate dyes the alum used must be of extreme purity. Samples containing even less than 0·001 p.c. of iron may be unsuitable for certain purposes. The percentage of iron in alum or in aluminium sulphate is usually

determined by means of a solution of ammonium thiocyanate standardised with iron alum. Many precautions are necessary in performing the analysis (*v.* Tatlock, J. Soc. Chem. Ind. 1887, 276; G. Lunge, Mon. Sci. 1897, 160).

Potassium alum crystallises with 24 molecules of water, in crystals belonging to the cubic system, usually in large colourless octahedra of sp.gr. 1·751 (Retgers, Zeitsch. physikal. Chem. 3, 289; J. B. 1889, 148).

De Boisbaudran has also obtained it crystallised with hemihedral faces of the tetrahedron. The crystalline form is affected by the presence of other substances in solution, and by the temperature. When formed at ordinary temperatures in the presence of basic alum, the crystals are cubes, frequently dull on the surface from the presence of the basic salt; for this reason Roman alum usually forms cubes. At 40°, even in presence of basic salts, octahedra are produced.

Potassium alum possesses the property of crystallising with hydrogen peroxide (Willstätter, Ber. 36, [1903] 1828).

According to Poggiale (Ann. Chim. Phys. [3] 8, 467), the solubility of potassium alum and of ammonium alum is as follows:—

100 parts water dissolve:

°C.	Crystallised Potassium alum	Crystallised Ammonium alum
0	3·9	5·2
10	9·5	9·1
20	15·1	13·6
30	22·0	19·3
40	30·9	27·3
50	44·1	36·5
60	66·6	51·3
70	90·7	72·0
80	134·5	103·0
90	209·3	187·8
100	357·5	421·9

Conductivity determinations, made on alum solutions of different concentrations, indicate that even at moderate dilutions the alum is resolved into its component salts.

Potassium alum possesses a sweetish astringent taste and a strongly acid reaction. The aqueous solution decomposes when heated, with precipitation of a basic alum, especially when dilute. For this reason a small quantity, not sufficient to be distinguished by taste, is frequently added to impure water. The gelatinous precipitate carries with it the colouring matter and most of the organic impurities, producing a slimy deposit.

Alum is almost insoluble in a saturated solution of aluminium sulphate, and is quite insoluble in alcohol. On exposure to air, the crystals become white on the surface. This change is due, not to the loss of water, but to the absorption of ammonia from the air, with formation of a basic salt. Below 30° they lose no water; at 42° they evolve 11 molecules (Juttke, Chem. Zentr. 18, 777). In a closed vessel over sulphuric acid they lose 18 molecules at 61° (Graham) and become slowly anhydrous at 100°, more rapidly in a current of air. Alum melts in its water of crystallisation at 92·5°, and when heated to dull redness is converted into a porous friable mass, slowly soluble in water, known as 'burnt alum.' At a white heat alumina and potassium sulphate alone remain.

When burnt alum is mixed with one-third its weight of carbon and heated to redness, the residue is spontaneously inflammable on account of the presence of finely divided potassium sulphide, and is known as Homberg's pyrophorus. By fusing alumina with potassium bisulphate and digesting the mass in warm water, anhydrous potassium alum may be obtained in crystals of which 5 parts are soluble in 100 of water at 10° and 74·5 parts at 100° (Salm-Horstmar, J. pr. Chem. 52, 319).

On the addition of caustic soda or sodium carbonate to a solution of alum until the precipitate at first produced is only just redissolved on agitation, *i.e.* when two-thirds of the acid has been neutralised, the solution contains a neutral basic alum, known as *neutral alum*, together with sodium sulphate. This solution, on account of the ease with which it gives up its excess of alumina to the fabric, is used by dyers as a mordant. Commercial potassium alum is frequently mixed with ammonium alum.

Alum is extensively used as a mordant in the dyeing industries, and in the production of other aluminium mordants such as the acetate, sulphoacetate, &c., employed in dyeing and printing and for shower-proofing fabrics. The alum used for dyeing with alizarin red must be free from iron, otherwise dull shades are produced. It is also employed in the manufacture of lake pigments, in the dressing of skins ('tawing') to produce white leather, in sizing paper, and in the production of fireproofing materials. In most of its applications, however, it is being replaced by aluminium sulphate, the use of which is considerably more economical.

Sodium alum, *Soda alum*

$$Na_2SO_4,Al_2O_3(SO_3)_3,24H_2O.$$

Occurs as *mendozite* in S. America and in Japan (Divers, Chem. News, 44, 218).

This alum was prepared by Zellner in 1816, by the spontaneous evaporation of a solution containing the sulphates of sodium and aluminium. Its existence, disputed by Ostwald, has been established by Wadmore (Chem. Soc. Proc. 21, 150; C.-B. 1905, 11, 18), who from a solution of the mixed sulphates obtained octahedral crystals having the above composition. From a hot concentrated solution it is deposited on cooling as a pasty mass which slowly becomes crystalline. Contrary to the statement frequently made, the crystals do not appreciably effloresce in the air.

Technically, sodium alum may be prepared in the following manner:—To a solution of aluminium sulphate containing 675 grams of the crystalline salt per litre, and maintained at a temperature of 50° to 60°, is added a solution of sodium sulphate containing 146 grams of the anhydrous salt per litre, until the liquid attains a density of 1·35; crystals of sodium alum separate on cooling. The crystallisation should be effected at a temperature between 10° and 25°; at 28° the formation of crystals proceeds very slowly, whilst below 10° separation of sodium sulphate occurs (Augé, D. R. P. 1899, 50323; J. 1890, 2635).

Messrs. F. M., D. D., and H. Spence (*Eng. Pat.* 1900, 5644) prepare a solution of sodium sulphate saturated at 40° to 50°, which is allowed to cool during agitation until a considerable proportion of decahydrated crystals have separated. The mixture of liquid and crystals is then run into a solution of aluminium sulphate containing the solid salt in suspension. There is thus obtained a large crop of well-defined soda alum crystals. Alternatively, the solid aluminium sulphate may be added to a suitable solution of sodium sulphate or chloride, in which either salt may be suspended in the solid state.

Sodium alum is much more soluble at ordinary temperatures than potassium or ammonium alum, in consequence of which it is more difficult to purify from iron. On account of the lower cost of sodium salts, it would be largely used in place of other and more expensive alums, if it could be easily purified by crystallisation (see *Eng. Pat.* 1881, 5650).

Sodium alum crystallises with 24 molecules of water in regular octahedra, having a sp.gr. of 1·667 (Soret). At 10·6° 100 parts of water dissolve 107·11 parts of the alum (Wadmore); according to Ure, the solution saturated at 15·5° contains 110 parts of the alum in 100 of water, and has a density of 1·296. Sodium alum is insoluble in alcohol.

Ammonium alum

$$(NH_4)_2SO_4,Al_2O_3(SO_3)_3,24H_2O$$

occurs as *Tschermigite* in Bohemia, and in the crater of Mount Etna.

Its preparation is analogous to that of potassium alum, a solution of aluminium sulphate, prepared by any of the methods already described, being treated with the equivalent quantity of ammonium sulphate, and the alum separated and purified by crystallisation.

Ammonium alum crystallises with 24 molecules of water in regular octahedra, having a conchoidal fracture and a density of 1·631 (Soret). At ordinary temperatures it is less soluble in water than potassium alum (*v.* Table of solubilities, under Potassium alum). The saturated solution boils at 110·6°, and contains 207·7 parts of the alum to 100 parts of water (Mulder). When heated the crystals swell up and form a porous mass, losing water and sulphuric acid; at a high temperature alumina alone remains. This serves as a useful method for the production of very pure alumina.

In its general properties and uses, ammonium alum closely resembles the corresponding potassium compound.

Aluminium sulphite $Al_2O_3(SO_2)_3$.

The bisulphite has been used by Becker (Dingl. poly. J. 257, 300), Suchomel (J. Soc. Chem. Ind. 1887, 143) and others, for the purification of beet sugars. Becker prepares for this purpose a solution of sp.gr. 1·167 containing 4·37 p.c. alumina and 13·9 p.c. sulphurous oxide, by dissolving the hydrated oxide in sulphurous acid.

Aluminium phosphates. As hydrated phosphate, aluminium occurs in the *turquoise*, and enters into the composition of *wavellite*, *lazulite* and *gibbsite*. It is found in considerable quantity in mineral phosphates, as in the Redonda phosphates which have been used for the preparation of alum and for fertilisers (*v.* ALUMS; MANURES). A massive stony variety is found on the island of Anguilla in the West Indies.

Aluminium thiocyanate or sulphocyanate has been proposed as a substitute for aluminium acetate for alizarin, steam reds, &c.; the colours produced are said to be especially permanent (*v.* Storch and Ströbel, Dingl. poly. J. 241, 464; and Gottlieb Stein, Dingl. poly. J. 250, 36).

Lauber and Haussmann (Dingl. poly. J. 245, 306) recommend the following method of preparation: 5 kilos. aluminium sulphate are dissolved in 5 litres boiling water, 250 grams of chalk are added, followed by 11·5 litres of crude calcium thiocyanate solution of 30°Tw., and the whole well stirred and allowed to settle. The clear liquid is ready for use.

Aluminium permanganate *v.* MANGANESE.

Aluminium silicates. These compounds are exceedingly numerous and important. As an anhydrous silicate, with silicate of iron, calcium, magnesium, &c., aluminium occurs in the varieties of *garnet*, crystallising in the regular system. As silicate of aluminium, calcium, and sodium it is found in *lapis-lazuli*, which was formerly used as *ultramarine*. It is now replaced by artificial ultramarine (*v.* ULTRAMARINE). As silicate of aluminium, combined with potassium, iron, and magnesium, it occurs in the *micas*. As double silicate of aluminium, potassium, sodium, magnesium, or calcium, it forms the varieties of *felspar* which occur in immense quantities in eruptive rocks. By the decomposition of felspar by the carbonic acid in the atmosphere and in rain or spring water, the alkaline compounds are removed, leaving clay of more or less purity (*v.* CLAY), which, under pressure, becomes hardened and laminated, forming *shale*, and finally *slate* (*q.v.*). Many of the silicates of aluminium are of great importance, and of the widest application. The more important of them are specially considered under their applications (*v.* POTTERY; PORCELAIN).

Aluminium acetate. *Red liquor* (*v. Aluminium acetates*, art. ACETIC ACID).

The compounds of aluminium with the higher fatty acids are used for increasing the viscosity of mineral lubricating oils, under the names 'oil pulp' and 'fluid gelatin' (L. Marquardt, Zeitsch. anal. Chem. 25, 159).

Aluminium oleate is a soft white, putty-like substance, of great tenacity, insoluble in water, soluble in ether and petroleum. A mixture of oleate, palmitate, and other fatty salts is produced from whale, cotton-seed, and similar oils by saponification with soda and addition of the sodium salt so produced to a solution of alum. The gummy precipitate is known as 'oil pulp,' and is dissolved in 4 or 5 parts of mineral oil to form a 'thickener' for addition to the lubricator. A sample of oil pulp resembling thick gelatin had a sp.gr. of 0·921, and contained 6 p.c. alumina combined with 30 p.c. fatty acids, together with 15 p.c. lard oil, and 48 p.c. paraffin oil (Oil and Colourman's Journ. 4, 403).

Aluminium palmitate is a constituent of oil pulp. It may be prepared in the same manner as the oleate, from palm oil. It forms a resinous, elastic, inodorous, neutral substance, insoluble in water, but readily soluble in petroleum and turpentine. K. Lieber (Dingl. poly. J. 246, 155) recommends the use of the latter solution as a varnish. It imparts a glossy appearance to

paper, leather, &c., and renders them waterproof without affecting their elasticity. G. H. B.

ALUMNOL *v.* SYNTHETIC DRUGS.

ALUM-SHALE. A kind of shale or slate containing disseminated iron pyrites, which, on prolonged exposure to the weather, gives aluminium sulphate, owing to the action of sulphuric acid (from the decomposition of the iron pyrites) on the clayey material. The heaps of weathered shale are leached with water, and to the solution of aluminium sulphate and sulphuric acid so obtained potashes are added. The alum obtained by the evaporation of this solution is purified by recrystallisation. The alum-shales of Liassic age on the coast of Yorkshire, in the neighbourhood of Whitby, have been largely worked by this method since the time of Queen Elizabeth, but now the industry has become extinct. Alum-shales in the coal-measures of the West Riding of Yorkshire are, however, still worked to a small extent (*v. Alums*, art. ALUMINIUM). L. J. S.

ALUNDUM. An abrasive manufactured at Niagara Falls from fused bauxite (*v.* ABRASIVES and BAUXITE).

ALUNITE or **ALUM-STONE.** Hydrated basic sulphate of aluminium and potassium $KAl_3(SO_4)_2(OH)_6$, usually found as white, compact, granular masses, somewhat resembling limestone in appearance. It mostly occurs in connection with volcanic rocks, having been formed by the action of solfataric vapours on such rocks. In some cases, however, it may have been formed by the action of decomposing iron-pyrites on clay. Extensive deposits are met with at Tolfa near Rome, in Tuscany and Hungary, and at Bulladelah in New South Wales. Alum is obtained from it by repeatedly roasting and lixiviating, the yield being from 60 to 80 p.c. In Hungary the harder and more compact varieties have been used for millstones. L. J. S.

ALUNOGEN. Hydrated aluminium sulphate $Al_2(SO_4)_3,18H_2O$, occurring as a white, delicately fibrous efflorescence on shale and other rocks. It has been formed by the action on the aluminous rock of the products of decomposition of iron pyrites. A trace of iron sulphate is often present, imparting a yellowish or reddish colour to the mineral. L. J. S.

ALVA or **ALFA** *v.* ESPARTO.

ALVELOS. A name applied to the *Euphorbia heterodoxa* (Muell.), growing in Brazil, the juice of which has been used as a cure for cancer (Pharm. J. [3] 15, 614).

ALYPIN. Trade name for *benzoyltetramethyldiaminoethyldimethylcarbinol hydrochloride.* Employed as an anæsthetic and as a remedy for vomiting and in the treatment of diseases of the upper respiratory passages and of the organ of hearing. Used also in veterinary practice in place of cocaine.

It occurs in crystals, m.p. 169°, sol. in water, forming a neutral solution. Aqueous solutions may be sterilised without undergoing decomposition by boiling from 5 to 10 minutes (Neustätter, Pharm. J. 1905, 869).

(For distinctive reactions, *v.* Lemaire, Rep. Pharm. 1906, 18, 385.) (*v.* SYNTHETIC DRUGS.)

AMADOU or **GERMAN TINDER.** (*Amadou*, Fr.; *Zunderschwamm*, Ger.) A spongy combustible substance, prepared from a species of fungus, *Fomes* (*Polyporus*) *igniarius*, the 'false' tinder-fungus, which grows on the trunks of the oak, but also on alder, willow, and various other trees. It must be plucked in the months of August and September. It may also be prepared from *Fomes* (*Polyporus*) *fomentarius*, the true tinder-fungus, also indigenous, found especially on the beech, elm, and various fruit trees. It was formerly used in surgery, and has hence been called surgeons' agaric. Amadou is prepared by removing the outer rind and carefully separating the yellow-brown spongy substance which lies within it. This substance is cut into thin slices, and beaten with a mallet to soften it, till it can be easily pulled asunder between the fingers. In this state it is useful in surgery. To convert it into tinder, it is boiled in a strong solution of nitre, dried, beaten anew, and put a second time into the solution. Sometimes, to render it very inflammable, it is imbued with gunpowder, whence the distinction of 'black' and 'brown' amadou.

AMALGAM. An alloy of mercury with some other metal or metals.

There are four general methods for preparing amalgams.

1. Metallic mercury is brought into contact with the other metal, either in the solid or in a finely divided state at the ordinary or at a higher temperature. In this way amalgams of antimony, arsenic, bismuth, cadmium, magnesium, potassium, silver, sodium, tellurium, thorium, tin, zinc, and lead may be obtained.

2. Mercury is brought into contact with a saturated solution of a salt of the metal, when part of the mercury goes into solution and the remainder combines with the liberated metal; or better still, zinc or sodium amalgam is employed, when the zinc or sodium displaces the metal in the solution. By this method amalgams of bismuth, calcium, chromium, iridium, iron, magnesium, manganese, osmium, palladium, and strontium may be prepared by using sodium amalgam, and cobalt and nickel by using zinc amalgam (Moissan, Compt. rend. 1879; Chem. News, 39, 84).

3. The metal to be amalgamated is placed in a solution of a mercury salt; copper may be amalgamated by this process.

4. The metal is placed in contact with mercury and dilute acid; this is the method usually employed in amalgamating zinc. Iron, aluminium, palladium, nickel, and cobalt may be made to combine with mercury by this process if they be placed in contact with a stick of zinc (Casamajor, Chem. News, 34, 36; Arch. Pharm. [3] 11, 64; Chem. Soc. Trans. [2] 34, 474).

Amalgams are also formed when mercury is used as the cathode in the electrolysis of salt solutions; a number of metals can thus be obtained as amalgams, although they cannot be obtained directly in the free state by the electrolysis of aqueous solutions.

The combination of sodium with mercury by method 1 takes place with great energy, heat and light being produced. It is best prepared by combining a small portion of the mercury with the sodium, and then adding the remainder to the amalgam.

Native amalgams are found in various parts of the world. The following table contains the analyses of a few:—

Ag	Hg	Au	Fe_2O_3	CaO	AgCl	Fe	Zn	Pb	$CaCO_3$	Cu	Insol. and loss	Locality	Analyst and reference
75·900	23·065	—	—	—	—	—	—	—	—	—	0·490	Kongsberg, Norway.	Flight, Phil. Mag. [5] 9, 146.
92·454	7·195	—	0·033	0·055	0·088	—	—	—	—	—	1·328	,,	,,
36·0	64·0	—	—	—	—	—	—	—	—	—	—	Moschellandsberg Palatinate.	Klaproth, Ure 1.
25·0	73·3	—	—	—	—	—	—	—	—	—	—	,,	Heyer, *id.*
27·5	72·5	—	—	—	—	—	—	—	—	—	—	Allemont, Dauphiné.	Cordier, *ib.*
46·30	51·12	—	—	—	—	0·18	tr.	tr.	0·21	—	1·01	Salagrube, Sweden.	Nordsbröm, J. 35, 1, 521.
56·70	43·27	—	—	—	—	—	—	—	—	tr.	—	Friedrichssegen.—Mine.	Weiss, J. 36, 1828; Z. geol. Ges. 34, 817.
—	60·98 to 58·37	39·02 to 41·63	—	—	—	—	—	—	—	—	—	Mariposa, California.	Ure.
5·00	57·40	38·39	—	—	—	—	—	—	—	—	—	Choco, New Grenada.	Schneider. Ure.

Gold and silver in the metallic state can be extracted from their ores by grinding the ores and making them pass through mercury, although this process is now largely replaced by the modern cyaniding methods. (For details, *v.* these metals; and May, J. Soc. Chem. Ind. 4, 352; Moon, *id.* 4, 678; Miller, *id.* 4, 122; Whitehead, *id.* 4, 503; Fisher and Waber, *id.* 4, 351; Barker, Dingl. poly. J. 251, 32; Body, *id.* 252, 33; Molloy, *id.* 254, 210; Bonnet, *id.* 254, 297; Cassel, *id.* 257, 286; Jordan, *id.* 258, 163; Hollick, *id.* 258, 168.) When the mercury has taken up a quantity of gold, the amalgam is squeezed through chamois leather, when the greater portion of the gold is left, combined with a little mercury, as a pasty mass. Kazantseff (Bull. Soc. chim. [2] 30, 20; Chem. Soc. Trans. [2] 34, 937) finds that the mercury which escapes contains at ordinary temperatures 0·126 p.c. of gold, at 0° 0·110 p.c., and at 100° 0·650 p.c., thus behaving like an aqueous solution.

Berthelot found that the solution of definite amalgams in different quantities of mercury, like the solution of salts in water, absorbs a constant amount of heat; thus the heat of solution of an amalgam of which the composition corresponds with the formula $Hg_{24}K$ in four times its weight of mercury is −8·0 kil. deg. of heat, and in twenty times −9·0 kil. deg. (Compt. rend. 89, 465; Chem. Soc. Abstr. 38, 1).

According to Berthelot, the maximum heats of formation for amalgams of potassium and sodium are 34·2 and 21·1, corresponding with crystalline amalgams containing 1·6 p.c. of potassium, and 2 p.c. of sodium respectively. In these amalgams the relative affinities of the free alkali metals are inverted: this explains Kraut's and Popp's observation that sodium displaces potassium when potassium hydroxide is treated with sodium amalgam, the final result being the formation of an amalgam of composition $Hg_{24}Na$ (Compt. rend. 88, 1335).

The views formerly held on the constitution of amalgams and particularly on the existence of definite amalgams of the nature of chemical compounds of mercury and the alloyed metal, have been profoundly modified by the study of these bodies by the methods of metallography (*v.* METALLOGRAPHY). The amalgams are found to be strictly analogous to other alloys, but their peculiar behaviour arises from the fact that they are frequently met with in a range of temperature which lies between the commencement of solidification and final complete crystallisation. It has been shown that a number of supposed compounds, of which the existence had been assumed on the ground that amalgams representing them took the form of homogeneous crystalline bodies, are not true compounds, whilst definite compounds of different composition have been found. Thus, in the case of sodium and potassium amalgams, the compounds Hg_4Na, Hg_2Na, $HgNa$, Hg_2Na_3, Hg_2Na_5, $HgNa_3$, and Hg_2K, HgK, Hg_3K, Hg_9K_2, and Hg_3K, have been recognised (Schüller, Zeitsch. anorg. Chem. 1904, 40, 385; Kurnakoff, *ibid.* 1900, 23, 439; Jaenecke, Zeitsch. physical. Chem. 1907, 58, 245).

The amalgams of bismuth, zinc, tin, and thallium are found not to contain any definite compounds (Pushin, Zeitsch. anorg. Chem. 1903, 36, 201; Heteren, *ibid.* 1904, 42, 129; Kurnakoff and Pushin, *ibid.* 1903, 30, 86).

'Ammonium amalgam' is prepared by acting on a saturated solution of ammonium chloride with sodium amalgam; the amalgam thus obtained soon breaks up into mercury, and ammonia and hydrogen gases. According to Wetherill (Amer. J. Sci. [2] 50. 160), this compound is not a true amalgam, as when an ammoniacal solution is electrolysed, the negative pole being a spongy plate impregnated with mercury, no amalgam is formed. Landolt (Zeitsch. f. Chem. [2] 5, 429) draws attention to the fact that ammonium amalgam does not reduce solutions of silver nitrate, ferric chloride, or cupric sulphate, as do sodium and potassium amalgams.

Seeley (Chem. News, 21, 265) has shown that on submitting ammonium amalgam to pressure, its volume diminishes in the same way that gases do, and hence he considers that the ammonia and hydrogen exist in the amalgam as gas, and that the spongy mass is only a froth of mercury inclosing these gases.

Gellatlin (Zeitsch. f. Chem. [2] 5, 607) asserts that when ammonium amalgam, free from sodium, is placed in contact with phosphorus, phosphoretted hydrogen is evolved, and he infers that the hydrogen must be in the nascent state.

Pfeil and Lippmann (Compt. rend. 62, 426) state that trimethylamine hydrochloride also forms a spongy amalgam which quickly decomposes with evolution of hydrogen and formation

of trimethylamine; saturated solutions of the hydrochlorides of aniline, coniine, morphine, and quinine give off hydrogen only.

Electrical amalgam is made by melting together 1 part of zinc and 1 part of tin, and then adding 3 parts of mercury. An amalgam of cadmium is used in the construction of the cadmium standard cell; this amalgam and its electrical behaviour have been studied by F. E. Smith (Phil. Mag. February, 1910).

Silvering amalgams. For metals, 1 part of silver to 8 parts of mercury; for glass, 1 part each of lead and tin, 2 parts bismuth, and 4 parts mercury. The use of amalgams for silvering has been almost completely superseded by the use—in the case of glass—of chemically deposited silver, and in the case of metals by electro-plating.

Teeth fillings. 1. Copper precipitated from copper sulphate solution with zinc, washed with sulphuric acid containing a small quantity of mercuric nitrate, and amalgamated with twice its weight of mercury (Fletcher), has the property of softening with heat and hardening again after a few hours. It is a permanent filling, as the copper salts penetrate and preserve the tooth substance. It has the objection of staining the tooth, and is only used in posterior teeth. 2. A palladium amalgam is sometimes employed, but its rapidity of setting, intense black colour, and cost are against its general use. 3. An alloy of silver 68·5, tin 25·5, gold 5, and zinc 1 p.c. (Black); or silver 69·5, tin 25·5, gold 4, and zinc 1 p.c. (Tulloch), amalgamated with mercury, is extensively employed, as it has a good edge strength, and suffers little, if any, shrinkage. The shrinkage is the greatest difficulty to overcome in order to render alloys of permanent use for teeth filling, the object being to secure such a proportion of metals that the shrinkage of one may be overcome by the expansion of another, and so obtain a watertight plug.

AMALIC ACID *v.* ALLOXANTIN.

AMANITA MUSCARIA. *Fly agaric.* A poisonous fungus, used in Kamtschatka and Siberia as a narcotic and intoxicant, and, when steeped in milk, as a fly-poison. A narcotic organic base, *muscarine* $C_5H_{15}NO_3$, which is the hydrated aldehyde of betaïne, has been isolated from it (Schmiedeberg and Harnack, J. 1876, 804).

The natural muscarine is like the artificial product in crystalline form, solubility, and composition of its platino- and auro-chlorides, and to a large extent in its physiological action, but unlike the artificial muscarine it does not induce paralysis of the intermuscular nerve-terminations in the frog, and myosis in the pupils of the eyes of birds (Nothnagel, Ber. 26, 801). It differs both in constitution and properties from anhydro- and *iso*-muscarine.

A green and red dye of composition $C_{29}H_{20}O_{10}$, and $C_{19}H_{18}O_6$ respectively, have also been isolated from it (Griffiths, Compt. rend. 130, 42).

AMARANTH *v.* AZO- COLOURING MATTERS.

AMAZON-STONE. A bright-green variety of the potash-felspar microcline ($KAlSi_3O_8$). It is found in granitic rocks near Lake Ilmen in the Ural Mountains, at Pike's Peak in Colorado, and recently of very good quality in Madagascar. It is used to a limited extent as a gem-stone, and for making various small ornamental objects (*v.* FELSPAR). L. J. S.

AMBAR LIQUID *v.* BALSAMS.

AMBER or **SUCCINITE.** (*Bernstein*, Ger.) A fossil resin derived from the extinct conifer *Pinites succinifer* (Göppert), and found as irregular nodules in strata of Tertiary age, principally on the Prussian coast of the Baltic. The amber-bearing stratum lies partly below sea-level, and the amber washed out by the action of the waves is picked up on the sea-shore or won by dredging. Such 'strand-amber' was formerly collected farther west, as far as the coast of Holland, and isolated specimens are picked up on the east coast of England (Norfolk, Suffolk, and Essex). At the present time the bulk of Prussian or Baltic amber is obtained from pits and mines in the 'blue earth' in Samland, East Prussia. Here the production in 1907 amounted to 404,300 kilos. and in addition about 20,000 kilos was collected on the sea-shore.

Baltic amber differs from other fossil resins in containing succinic acid, which is present to the extent of 3 to 4 p.c. in perfectly transparent specimens, but reaching 8 p.c. in cloudy ('frothy') amber. It is therefore distinguished by the mineralogical name *succinite*, and in the trade the tendency is to apply the name 'amber' exclusively to Baltic amber. The composition is somewhat variable, averaging C, 79 p.c.; O, 10·5 p.c.; H, 10·5 p.c.; and corresponding approximately with the formula $C_{10}H_{16}O$. Sulphur is also present (0·26 to 0·42 p.c.), and some ash, usually about 0·2 p.c., but increasing in amount if the material encloses foreign matter. Amber is, however, not a simple resin; when heated, it gives oil of amber (*q.v.*) and other products, and by the action of solvents at least four different kinds of resin can be extracted from it. According to O. Helm, Baltic amber contains 17 to 22 p.c. of a resin (m.p. 105°) soluble in alcohol; 5 to 6 p.c. of a resin (m.p. 145°) insoluble in alcohol, but soluble in ether; 7 to 9 p.c. of a resin (m.p. 175°) insoluble in alcohol and ether, but dissolving in caustic potash; and 44 to 60 p.c. of insoluble bitumen.

Baltic amber is usually pale yellow, ranging to brown or reddish-brown in colour, and it varies from perfect transparency to opacity. The varying degrees of turbidity are due to the presence of vast numbers of microscopic air-bubbles. The enclosure of insects and fragments of wood and dirt in amber is well known, and points at once to the mode of origin of the material. According to differences in colour and transparency, various trade names are applied, such as 'clear,' 'flohmig,' 'cloudy,' 'bastard,' 'osseous' or 'bone,' and 'frothy.' The sp.gr. ranges from 1·05 to 1·10 (varying with the porosity); and the hardness is 2½, being rather higher than that of most other resins, which latter can be scratched with the finger-nail. The material is brittle and breaks with a conchoidal fracture. When cut with a knife, parings are not obtained, but only powder. It can be turned on the lathe and takes a good polish, being worked with whiting and water or rotten-stone and oil, and finished by friction with a flannel. When heated, amber begins to soften at about 150°, giving a characteristic odour; it melts at 350°–375°, that is, at a higher temperature than other resins, giving dense white fumes with a peculiar aromatic odour, and causing violent coughing. When rubbed it

becomes negatively electrified (from the ancient name *electron*, for amber, the word 'electricity' is derived); and when rubbed vigorously it emits an aromatic odour, but does not become sticky like other resins. These characters serve to distinguish true amber from the more abundant copal; the latter is further usually clearer, lighter in colour, and more gummy in appearance.

In the trade the material is sorted into many grades suited for various purposes. The larger pieces of better quality ('work-stone') are cut into beads and other small personal ornaments, and are largely used for making the mouth-pieces of tobacco-pipes and cigar- and cigarette-holders. Smaller and impure fragments ('varnish') are melted down for the manufacture of amber varnish and lac; but in recent years such material is largely converted by the application of heat and hydraulic pressure into blocks of *pressed amber* or 'ambroid.' About 35,000 kilos. of pressed amber is now produced annually from three times the amount of rough amber; it is cut for ornaments and smokers' mouth-pieces. Prices (current in 1908) for rough 'work-stone' vary from 11*l.* to 10*s.* per kilo, and for smaller, inferior material ('varnish') about 5*s.* per kilo. Pressed amber fetches 4*l.* to 5*l.* per kilo. The production and the trade in amber, as well as the literature of the subject, is almost exclusively German, though the finished articles are largely made in Vienna.

Other varieties of fossil resin closely allied to amber, but regarded as distinct from Prussian or Baltic amber (succinite), are the following:—

Beckerite (E. Pieszczek, 1880), a black resin occurring with Prussian amber.

Burmite, Birmite, or Burmese amber (F. Noetling, 1893), a dark reddish-brown, amber-like resin, which has long been mined in Upper Burma and used in China. It is found in large masses, one seen by the writer weighing 33½ lbs., whilst the largest piece of Prussian amber yet found weighs only 9·7 kilos. (21⅓ lbs.).

Chemawinite (B. J. Harrington, 1891), Cedarite (R. Klebs, 1897), or Canadian amber, found as pale yellow fragments the size of a pea to that of a walnut on the beach of Cedar Lake, near Chemahawin in Saskatchewan.

Gedrite (O. Helm, 1878), a brittle, pale yellow resin found with Prussian amber, but differing from this in containing less oxygen and no succinic acid; m.p. 140°.

Glessite (O. Helm, 1881), also found with Prussian amber; it contains no succinic acid, but probably some formic acid; m.p. 200°.

Roumanite, Romanite, Rumänite, or Roumanian amber (O. Helm, 1891), a brownish-yellow to brown resin, found in Tertiary sandstone at several places in Roumania; it resembles Prussian amber in containing some succinic acid (0·3–3·2 p.c.), and is characterised by the relatively large amount of sulphur (1·15 p.c.); m.p. 300°.

Simetite, or Sicilian amber (O. Helm and H. Conwentz, 1886), a clear wine-red to garnet-red resin, remarkable for its beautiful green or blue fluorescence, found in the river Simeto and other parts of Sicily. It contains only 0·4 p.c. of succinic acid.

Stantienite (E. Pieszczek, 1880), a brown resin occurring with Prussian amber.

For several papers on amber and amber-like resins, by O. Helm and by P. Dahms, see Schr. natf. Ges. Danzig, vols. iv.–xii. (1878–1908). See also Max Bauer, Edelsteinkunde, 2nd edit. 1909, and English transl. (Precious Stones), by L. J. Spencer, 1904. L. J. S.

AMBER, OIL OF. When amber is heated it softens, fuses, and gives off succinic acid, water, oil, and a combustible gas. If the residue (colophony of amber) be more strongly heated, a colourless oil passes over. These oils, according to Pelletier and Walter (Ann. Chem. Phys. [3] 9, 89), have the composition of oil of turpentine. By distilling with water, a pale-yellow oil, having a strong odour and acrid taste, can be obtained. It blackens and thickens on exposure to air and heat, boils at 86°, and has a sp.gr. of 0·758 at 24°. One part of the rectified oil mixed with 24 parts of alcohol (0·830) and 96 of ammonia, forms *eau de luce*, a celebrated old perfume. By mixing 'eau de luce' with nitric acid, artificial musk is made. Its solution in alcohol was formerly considered as a specific for whooping-cough (*v.* also Oils, Essential, and Resins).

AMBER VARNISH *v.* Varnish.

AMBERGRIS. (*Ambregris*, Fr.; *Ambra*, *Ambar*, Ger.) (J. Soc. Chem. Ind. 1890, 429.) Is found in the sea, near the coasts of tropical countries, and in the intestines of the spermaceti whale (*Physeter macrocephalus*).

Ambergris is generally found in fragments, but a piece has been obtained weighing 225 lbs. Its sp.gr. ranges from 0·780 to 0·926 (0·780 to 0·896 Brande, 0·908 to 0·920 Pereira). If of good quality, it adheres like wax to the edge of a knife with which it is scraped, retains the impression of the nails, and emits a fat odoriferous liquid on being penetrated with a hot needle. It is generally brittle, but on rubbing it with the nail it becomes smooth like hard soap. Its colour varies from black to white. Its smell is peculiar, and not easily counterfeited. It melts at 62·2°, at 100° it is volatilised as a white vapour; on a red-hot coal it burns and is entirely dissipated. Water has no action on it; acids, except nitric acid, act feebly upon it; ether and the volatile oils dissolve it; so do the fixed oils, and also ammonia when assisted by heat; alcohol dissolves a portion of it.

The principal constituent of ambergris is *ambrein* (*q.v.*); its inorganic constituents are carbonate and phosphate of calcium, with traces of ferric oxide and alkaline chlorides.

Used by perfumers. The Chinese test its purity by scraping it upon boiling tea, in which it should wholly melt.

AMBERITE *v.* Explosives.

AMBLYGONITE. Fluo-phosphate of aluminium and lithium $AlPO_4,LiF$, crystallising in the anorthic system. It is usually found as whitish cleavage masses much resembling felspar in appearance, from which it is distinguished by its higher sp.gr. 3·01–3·09 and chemical characters. It occurs in granitic rocks at Montebras in France, Cácares in Spain, Pala in California, &c. At each of the places named it has been mined for the preparation of lithium salts, the phosphate being a by-product. It contains about 10 p.c. of lithia. L. J. S.

AMBREÏN. (*Ambreine*, Fr.; *Ambarstoff*, Ger.) Isolated by Pelletier and Caventou, by digesting ambergris in hot alcohol, sp.gr. 0·827. It is of a brilliant white colour, has an agreeable odour, is destitute of taste, is insoluble in water, dissolves readily in alcohol and ether. Melts at 36°, and is volatilised above 100°; is non-saponifiable; is converted by nitric acid into *ambreic* acid. Ambreïn is probably impure cholesterol. Pelletier (Annalen, 6, 24) found it to contain C 83·3, H 13·3, and O 3·31 p.c.

AMBRITE. A brown translucent resin, similar to retinite, found in association with New Zealand coal.

AMENYL. Trade name for the *hydrochloride* of *methyl hydrastimide*. Forms yellowish needles, m.p. 227°. Soluble in hot water or alcohol.

AMERICAN COW or MILK TREE WAX *v.* WAX.

AMERICAN ELEMI *v.* OLEO-RESINS.

AMETHYST. A purple transparent variety of crystallised quartz (SiO_2), used as a gem-stone. So named, from ἀμέθυστος, 'not drunken,' owing to the ancient belief that the stone when worn as a charm prevented intoxication (*v.* QUARTZ). L. J. S.

AMETHYST. Tetramethyl safranine and tetraamyl safranine are found in commerce under this name (*v.* AZINES).

AMETHYST, ORIENTAL, *v.* CORUNDUM.

AMIANTHUS (*Amiante*, Fr.) *Mountain flax* (*v.* ASBESTOS).

AMIDASE *v.* ENZYMES.

AMIDE POWDER. An explosive similar to ordinary gunpowder, in which, in place of the sulphur, an ammonium salt is employed in combination with saltpetre, in such proportions that on ignition potassamide, volatile at high temperatures, is formed. This increases the useful effect of the explosive, which burns without residue (Gaens. Eng. Pat. 14412, 1885; J. Soc. Chem. Ind. 5, 678).

AMIDOAZOBENZENE or ANILINE YELLOW *v.* AZO- COLOURING MATTERS.

AMIDOGENE. An explosive made by dissolving 73 parts of potassium nitrate and 1 part magnesium sulphate in one-third their weight of boiling water; 8 parts of ground wood charcoal, 8 parts of bran, and 10 parts of sulphur are added, and the whole is digested for two hours at 140°; it is then dried at 50° and made into cartridges (Gemperle, J. Soc. Chem. Ind. 3, 191; 1, 201; Biedermann's Chem. Tech. Jahrb. 7, 146).

AMIDOGUANIDINE *v.* HYDRAZINES.

AMIDOL. Trade name for 2:4-diaminophenol hydrochloride, used as a photographic developer.

AMIDONAPHTHOLS *v.* AZO- COLOURING MATTERS.

AMIDONAPHTHOPHENAZINE *v.* AZINES.

AMIDOPHENOPHENANTHRAZINE *v.* AZINES.

AMINES. Amines or 'ammonia bases' may be regarded as substances derived from ammonia by the substitution of hydrocarbon radicles for hydrogen. They may also be looked upon as derived from hydrocarbons by the replacement of one or more hydrogen atoms by NH_2 or its alkyl substitution products NHR or NRR'. The definition of the term would include alkyl derivatives of hydrazine and hydrazoic acid, and compounds such as nitrosamines, diazo- compounds; and others which contain nitrogen linked to nitrogen or elements other than carbon, as well as to alkyl- residues. It also includes compounds in which the nitrogen forms part of a ring, as in pyridine, pyrrol, and their derivatives, among which the alkaloids may be mentioned. The majority of these more complex substances are treated of in detail in special articles (see arts. AZO- COLOURING MATTERS; AZINES; VEGETABLE ALKALOIDS; BONE OIL; QUINOLINE, &c.), and come within the scope of this only in so far as they possess the general characteristics of the ammonia bases.

Amines are classed as primary, secondary, or tertiary, according as one, two, or three of the hydrogen atoms of ammonia have been replaced by alkyl groups. Thus the general formula of the primary amines is NH_2R, of the secondary amines NHRR', and of the tertiary amines NRR'R'', where R, R', and R'' may be identical or represent different alkyl groups. The reactions of the amines differ to some extent according as the substituting alkyl- groups are (1) all aliphatic; (2) mixed aliphatic and aromatic, with the nitrogen attached to the aliphatic residue, as in benzylamine; (3) mixed aliphatic and aromatic, with the nitrogen attached to a carbon atom of the benzene ring, as in methyl aniline; and (4) pure aromatic amines such as aniline itself, di- and tri-phenylamine, and their homologues. Substances of groups (1) and (2) will be referred to here as aliphatic and aromatic amines respectively, and those of groups (3) and (4) as aromatic amino- compounds. Aromatic amino- compounds serve as the starting materials in many of the different branches of the dyeing industry, and are prepared artificially in large quantities (*see* arts. ANILINE; AZO- COLOURING MATTERS; TRIPHENYLMETHANE COLOURING MATTERS; DIPHENYLAMINE, &c.).

With the important exception of the vegetable alkaloids, the amines are not widely distributed in nature, though some of the lower members of the fatty series (methylamines) occur in plants and in the blood of some animals. They are, however, found as decomposition products of animal and vegetable organisms, and of mineral substances. Thus the methylamines are found in herring brine and in decomposing fish. Others, chiefly diamines, are found in certain pathological conditions of the urine, and as decomposition products of the animal tissues (ptomaines). The decomposition of proteins gives rise to large numbers of amino-acids. Aniline was first isolated as a product of the distillation of indigo, and it and its homologues as well as other bases are present in the distillates from bone oil (Dippel's oil), and of coal tar. A mixture of fatty amines is obtained in the dry distillation of the residues in the beet-sugar industry, and this, under the name of 'trimethylamine,' of which it contains about 5 p.c., is used in France for the preparation for industrial purposes of methyl chloride; on account of the greater solubility of its hydrochloride, it has also been used instead of ammonia in the preparation of potassium carbonate, in a manner analogous to the Solvay method for the preparation of sodium carbonate, but the process does not seem to have been commercially successful.

General methods of preparation.

1. *By action of ammonia or its alkyl derivatives on substitution products (generally haloid or hydroxyl derivatives) of hydrocarbons.*

The method first described by Hofmann (Phil. Trans. 1850, 1, 93; 1851, 2, 357), of heating alkyl halides (preferably bromides or iodides) with ammonia, is available for the preparation of primary, secondary, and tertiary amines of the fatty series, and if aniline is substituted for ammonia, for the preparation of secondary, tertiary, and aromatic amino compounds. Quaternary ammonium compounds are also formed in the reactions, which may be represented as follows:—

$$NH_3 + RBr = NH_2R \cdot HBr.$$
$$NH_2R + R'Br = NHRR' \cdot HBr.$$
$$NHRR' + R''Br = NRR'R'' \cdot HBr.$$
$$NRR'R'' + R'''Br = NRR'R''R'''Br.$$

The reaction will take place, though only very slowly, in water solution, more quickly in alcoholic solution, and best on heating in alcoholic solution in sealed tubes at 100°. The products obtained may contain haloid salts of one or all of the possible amines, and of the quaternary bases.

In the preparation on the large scale of secondary and tertiary aromatic amino- compounds, *e.g.* dimethylaniline, the primary amine is heated under pressure directly with the alcohol and hydrochloric or sulphuric acid at 180°–200°. Here the alkyl group is exchanged directly for hydrogen without the intermediate separation of the alkyl halide. The presence of other negative groups in the benzene molecule increases the ease with which the NH_2 group can displace halogen groups. Thus the chlorine atoms of chlorbenzene can be replaced by NH_2 groups by the action of ammonia if the benzene ring also contains NO_2 groups.

Amines may also be obtained by heating zinc ammonium chloride with alcohols at 250°–260° (Merz and Gasiorowski, Ber. 1884, 17, 623).

Alcohols or phenols will react with ammonia or its alkyl derivatives on heating in the presence of zinc chloride, calcium chloride, or other catalytic agent (Merz and Weith, Ber. 1880, 13, 1298; Merz and Mueller, Ber. 1886, 19, 2901).

Mixtures of the vapours of alcohol and ammonia or primary amine led through tubes containing finely divided thoria or tungsten oxide at 360° give amines (Sabatier and Mailhe, Compt. rend. 1908, 148, 898).

Sodamide or its alkyl substitution products may be used instead of ammonia in the case of aliphatic amines.

$$NH_2Na + CH_3Cl = NH_2 \cdot CH_3 + NaCl$$

(Lebeau, Compt. rend. 1905, 140, 1042; Chablay, Compt. rend. 1905, 140, 1262). Sodamide will also react with anhydrous sulphuric esters of the aliphatic series, and with aromatic sulphonic acids to give primary amines (Jackson and Wing, Ber. 1886, 19, 902; Titherley, Chem. Soc. Trans. 1901, 79, 399).

2. *By reduction of nitrogen-containing substances.*

This method is chiefly important in the preparation of primary amines, and particularly in that of the aromatic amino- compounds, the nitro-compounds of which are easily obtained by direct nitration of the hydrocarbons, whereas the nitro-compounds of the aliphatic and aromatic amines are only obtained indirectly. Zinin in 1842 prepared aniline from nitrobenzene, by the action of alcoholic ammoniun sulphide. On the commercial scale, as for instance in the preparation of aniline, iron and water with some hydrochloric acid is usually employed as the reducing agent. Nitro- compounds, however, as well as nitriles, oximes, and hydrazones, can be reduced to amines by electrolysis in dilute alcohol and sulphuric acid, using a nickel kathode (Pierron, Bull. Soc. chim. 1899, [3] 21, 780). A mixture of aliphatic aldehydes and ammonia is converted into amines if electrolysed in sulphuric acid solution with a lead kathode, the relative proportions of primary, secondary, and tertiary amines formed depending on the strength of the current, and the relative amounts of aldehyde and ammonia present (Knudsen, Ber. 1909, 42, 3994). Another method for the reduction of nitro compounds, nitriles, oximes, and hydrazones, consists in heating in a stream of hydrogen in the presence of finely divided nickel or copper (Sabatier and Senderens, Compt. rend. 1902, 125, 225). In all these methods the temperature must not be allowed to rise too high, or reduction of the amine to hydrocarbon and ammonia takes place. Other reducing agents employed are sodium amalgam and water, sodium and alcohol, sodium sulphide, zinc-dust and potash, stannous chloride, &c. Magnesium alkyl iodide (the Grignard reagent) sometimes acts as a reducing agent, and ethyl aniline has been obtained by treatment of nitrobenzene, with magnesium ethyl iodide (Oddo, Atti R. Accad. Lincei, 1904 (v.) 13, 2, 220).

Amides and amidines are also converted to amines by reduction with sodium and alcohol (Guerbet, Compt. rend. 1899, 129, 61).

$$RCONH_2 + 2H_2 = RCH \cdot NH_2 + H_2O.$$
$$RCNH \cdot NH_2 + 2H_2 = R \cdot CH_2 \cdot NH_2 + NH_3.$$

Condensation products of the action of primary amines and aldehydes of the type $R \cdot CH : N \cdot R'$, yield secondary amines on reduction.

$$R \cdot CH : NR' + H_2 = R \cdot CH_2 \cdot NHR'$$

(Stoermer and v. Lepel, Ber. 1896, 29, 2110; Brand, Ber. 1909, 42, 3460).

3. *From amides by the action of bromine and potash.* (Hofmann, Ber. 1882, 15, 762.)

This reaction is mainly applicable to the preparation of primary fatty amines, and gives good yields only with the lower members of the series. The first product of the reaction is a bromamide, and this on further treatment with potash gives amine, potassium bromide, and carbon dioxide, the alkyl group being transferred from the carbon to the nitrogen atom, as in the 'Beckman rearrangement.'

$$CH_3 \cdot CONH_2 + KOH + Br_2 = CH_3 \cdot CONHBr + KBr + H_2O.$$
$$CH_3 \cdot CONHBr + KOH = CH_3 \cdot NH_2 + CO_2 + KBr.$$

Azides on boiling with alcohol or water, and subsequent treatment with conc. HCl give amines.

$$R \cdot CO \cdot N_3 + C_2H_5 \cdot OH = RNH \cdot COOC_2H_5 + N_2.$$
$$R \cdot NH \cdot COOC_2H_5 + H_2O = RNH_2 + CO_2 + C_2H_5OH$$

(Curtius, Ber. 1894; 27, 779, 1896. 29, 1166).

4. *By the action of alkalis on alkyl isocyanates.* (Wurtz, Annalen, 1849, 71, 330; 1850, 76, 317.)

The interest of this method is mainly historical, since it led to the discovery of the amines by Wurtz in 1848. Primary amines are the chief product, but secondary and tertiary amines are also formed in small quantities.

$$C_2H_5NCO+H_2O = C_2H_5\cdot NH_2+CO_2.$$

5. *By hydrolysis of alkyl esters of thiocarbamines and isocyanides with concentrated acids.*

$$C_2H_5NCS+H_2O = C_2H_5\cdot NH_2+COS.$$
$$C_2H_5NC+H_2O = C_2H_5\cdot NH_2+HCOOH.$$

6. *From compounds which certain substances form with alkyl halides.*

(*a*) Hexamethylene tetramine, formed by the action of ammonia on formaldehyde, gives addition compounds of the type $C_6H_{12}N_4\cdot RI$ with alkyl iodides. These on treatment with HCl and alcohol are decomposed, giving primary amines (Delépine, Compt. rend. 1897, 124, 292; Ann. Chim. Phys. 1898, [7] 15, 508).

(*b*) Phthalimide, on treatment with alcoholic potash, gives potassium phthalimide, and this gives an alkyl derivative on treatment with alkyl iodide, which on hydrolysis with fuming HCl yields a primary amine.

$$C_6H_4(CO)_2NK+RI = C_6H_4(CO)_2NR+KI.$$
$$C_6H_4(CO)_2NR+2H_2O=C_6H_4(COOH)_2+NH_2R$$

(Gabriel, Ber. 1887, 20, 2224; 1891, 24, 3104).

(*c*) Magnesium alkyl iodides form addition compounds with phenyl *iso*cyanate; these, on treatment with water are converted into anilides, which yield amines on saponification (Blaise, Compt. rend. 1901, 132, 38, 478, 978).

(*d*) Sodium acetamide, if treated with alkyl iodide, gives mono- and di-alkyl derivatives of formula R·CONHR, and R·CONRR', and these on saponification yield primary and secondary amines respectively (Titherley, Chem. Soc. Trans. 1901, 79, 399).

7. *By distillation of amino- acids with baryta.*

$$CH_3CH\begin{matrix}COOH\\NH_2\end{matrix} = CH_3\cdot CH_2\cdot NH_2+CO_2.$$

8. *Aliphatic primary and secondary amines may be obtained by the action of potash on the p-nitroso derivatives of secondary and tertiary aromatic amino- compounds.*

$$NO\cdot N\cdot C_6H_4(CH_3)_2+KOH = C_6H_4\cdot NO\cdot OK+N(CH_3)_2H.$$
$$NO\cdot C_6H_4\cdot NHCH_3+KOH = C_6H_4\cdot NO\cdot OK+NH_2\cdot CH_3.$$

9. *Tertiary amines can be obtained by heating primary and secondary bases with excess of potassium alkyl sulphate.*

$$RR'NH+CH_3OSO_3K = RR'NCH_3+HOSO_3K.$$

General Properties.

The amines of the aliphatic series are volatile inflammable substances, the lower members being gases or liquids with low boiling-points, very soluble in water and strongly alkaline to litmus; the density of the liquid members of the series is about 0·75 that of water, and increases slightly with increase in the molecular weight. Their basicity, measured by the conductivity method, is considerably greater than that of ammonia, and they will saponify esters and precipitate oxides from the salts of many of the heavy metals. They have an ammoniacal and fishy odour. The smell, inflammability, boiling-point, and solubility in water become less with increase in the molecular weight, and the highest known members are odourless solids at ordinary temperatures. They react with moist air with formation of

ALIPHATIC AMINES.

Alkyl groups	Primary compounds			Secondary compounds		Tertiary compounds	
	M.pt.	B.pt.	Sp.gr.	B.pt.	Sp.gr.	B.pt.	Sp.gr.
Methyl	—	−6·7°	0·699 (−11°)	+7°	0·686 (−6°)	+3·5°	0·662 (−5°)
Ethyl	−83·8°	+19°	0·708 (−2°)	56°	0·711 (+15°)	90°	0·735 (+15°)
Propyl	—	49°	0·728 (0°)	110°	0·738 (20°)	156°	0·771 (0°)
iso-Propyl	—	32°	0·690 (18°)	84°	0·724 (15°)	—	—
prim. n-Butyl	—	77·8°	0·742 (15°)	160°	—	216·5°	0·791 (0°)
iso-Butyl	—	66°	0·735 (15°)	136°	—	187°	0·785 (21°)
sec. Butyl	—	63°	0·718 (20°)	—	—	—	—
tert. Butyl	—	43·8°	0·698 (15°)	—	—	—	—
prim. n-Amyl	—	104°	0·766 (19°)	—	—	—	—
iso-Amyl	—	95°	0·750 (18°)	187°	0·782 (0°)	235°	—
tert. Butyl-methyl	—	82°–83°	—	—	—	—	—
sec. n-Amyl	—	90°–91°	0·749 (20°)	—	—	—	—
sec. iso-Amyl	—	83°–84°	0·757 (18·5°)	—	—	—	—
tert. Amyl	—	78·5°	0·748 (15°)	—	—	—	—
prim. n-Hexyl	—	129°	—	—	—	260°	—
„ „ Heptyl	—	153°	0·777 (20°)	—	—	—	—
„ „ Octyl	—	175°–177°	0·777 (26·8°)	297°	—	366°	—
„ „ Nonyl	—	190°–192°	—	—	—	—	—
„ „ Decyl	+17	216°–218°	—	—	—	—	—
„ „ Undecyl	15°	232°	—	—	—	—	—
„ „ Duodecyl	27°	248°	—	—	—	—	—
„ „ Tridecyl	27°	265°	—	—	—	—	—
„ „ Tetradecyl	37°	162° (15 mm.)	—	—	—	—	—
„ „ Pentadecyl	36·5°	298°–301°	—	—	—	—	—
„ „ Hexadecyl	45°	187° (15 mm.)	—	—	—	—	—
„ „ Heptadecyl	49°	335°–340°	—	—	—	—	—

HOMOLOGUES OF ANILINE.

Primary aromatic amino- compounds						
Formula	Popular name	Systematic name	M.pt.	B.pt.	Sp. gr.	M. pt. of mono-acetyl deriv.
$C_6H_5 \cdot NH_2$	aniline	aminobenzene	−8°	183°	1·024 (16°)	115°
$CH_3 \cdot C_6H_4 \cdot NH_2$	ortho toluidine	1-methyl-2-aminobenzene	—	199°	0·999 (20°)	110°
	meta ,,	1-methyl-3-aminobenzene	—	199°	0·998 (25°)	65·5°
	para ,,	1-methyl-4-aminobenzene	+42·8°	198°	—	153°
$(CH_3)_2C_6H_3 \cdot NH_2$	1-2-3 ortho xylidine	1 : 2-dimethyl-3-aminobenzene	—	223°	0·991 (15°)	134°
	1-2-4 ,, ,,	1 : 2-dimethyl-4-aminobenzene	+49°	226°	1·076 (17°)	99°
	1-3-2 meta ,,	1 : 3-dimethyl-2-aminobenzene	—	215°	—	176·5°
	asymm. meta xylidine	1 : 3-dimethyl-4-aminobenzene	—	215°	0·918 (25°)	129°
	symm. meta xylidine	1 : 3-dimethyl-5-aminobenzene	—	223°	0·972 (15°)	140·5°
	para xylidine	1 : 4-dimethyl-2-aminobenzene	+15·5°	215°	0·980 (15°)	139·5°
$C_2H_5 \cdot C_6H_4 \cdot NH_2$	para amino ethyl benzene	1-ethyl-4-amino-benzene	−5°	214°	0·975 (22°)	94·5°
$(CH_3)_3C_6H_2 \cdot NH_2$	mesidine	1 : 3 : 5-trimethyl-2-aminobenzene	—	233°	—	216°
	pseudo-cumidine	1 : 2 : 4-trimethyl-5-aminobenzene	+68°	234°	—	164°
$(C_2H_5 \cdot CH_2)C_6H_4 \cdot NH_2$	para amino propyl benzene	1-propyl-4-aminobenzene	—	225°	—	—
$(CH_3)_2CH \cdot C_6H_4 \cdot NH_2$	cumidine	1-*iso*propyl-4-aminobenzene	—	218°	—	102·5°
$(CH_3)_4C_6H \cdot NH_2$	prehnidine	1 : 2 : 3 : 4-tetramethyl-5-aminobenzene	+70°	260°	—	172°
	isoduridine	1 : 2 : 3 : 5-tetramethyl-4-aminobenzene	+24°	255°	0·978 (24°)	215°
$(CH_3)(C_3H_7)C_6H_3 \cdot NH_2$	carvacrylamine	1-methyl-4-*iso*propyl-2-aminobenzene	—	241°	0·944 (24°)	72°
	thymylamine	1-methyl-4-*iso*propyl-3-aminobenzene	—	230°	—	112·5°
$(CH_3)_2CH \cdot CH_2 \cdot C_6H_4 \cdot NH_2$	para amino *iso*butyl benzene	1-*iso*butyl-4-aminobenzene	+17°	230°	0·937 (25°)	170°
$(CH_3)_5C_6 \cdot NH_2$	amino pentamethyl benzene	pentamethyl aminobenzene	152°	278°	—	213°
$C_5H_{11} \cdot C_6H_4 \cdot NH_2$	amino *iso*amyl benzene	—	—	260°	—	—
$C_8H_{17} \cdot C_6H_4 \cdot NH_2$	para amino octyl benzene	1-octyl-4-aminobenzene	+19·5°	310°	—	93°
$C_{16}H_{33} \cdot C_6H_4 \cdot NH_2$	amino cetyl benzene	hexadecyl aminobenzene	53°	255° (14 mm.)	—	104°
$C_{18}H_{37} \cdot C_6H_4NH_2$	amino octadecyl benzene	octadecyl aminobenzene	61°	274° (15 mm.)	—	—

carbonates. Aromatic amines (benzylamine and its homologues) closely resemble the aliphatic amines, but are not quite so strongly basic in character, owing to the presence of the negative phenyl group. The aromatic amino- compounds (aniline and its homologues) are less basic than ammonia, and the basicity diminishes with increase of the number of phenyl- groups attached to the nitrogen atom. Thus the salts of diphenylamine are hydrolysed by water to a greater extent than those of aniline, whilst triphenylamine is a neutral body and forms no salts with acids. Comparatively few amines are known which contain only aromatic groups; of these aniline and diphenylamine are prepared on the large scale in the dyeing industry, as well as many secondary and tertiary amino compounds containing both fatty and aromatic groups.

The above lists of the chief homologues of methylamine and aniline (*see* pp. 129, 130) are taken from Meyer and Jacobsen's Lehrbuch der Organischen Chemie.

All classes of amines form addition products with acids, containing one molecule of base to one molecule of monobasic acid. Compounds containing three molecules of HCl to one of amine have also been obtained (Korczynski, Ber. 1908, 41, 4379). The picrates are specially characteristic, and are used for the identification of the amines, as are also the double salts with platinum and gold chlorides, which have the general formulæ $B_2H_2PtCl_6$ and $BHAuCl_4$ respectively. Many aliphatic amines form hydrates with one molecule of water of crystallisation. Double salts with mercuric chloride and stannic chloride, and with silver salts, crystallise well, and organic analogues of ammonium pyrophosphate and arsenate are known, but are not very stable (Brisac, Bull. Soc. chim. 1903, [3] 29, 591). With alkyl halides they form quaternary ammonium compounds of the type NRR′R″R‴I, where RR′R″R‴ may be the same or different radicles. In cases where these radicles are all different, the substances are capable of existing in two enantiomorphous optically active

forms, and a number of these have been isolated. The quaternary ammonium compounds, unlike their inorganic analogues, are not decomposed on boiling with potash; on heating alone they give tertiary amines and alkyl halides. The corresponding bases are obtained from their halides by treatment with moist silver oxide; they are strongly alkaline to litmus, and the solutions generally decompose easily on evaporation, but some of the aliphatic members have been obtained crystalline by evaporation *in vacuó*.

The formation of quaternary ammonium compounds by addition of excess of methyl iodide to an amine gives a quantitative method for the determination of the number of replaceable hydrogen atoms in the substance. Analysis of the original compound and of its quaternary methyl derivative gives the number of methyl groups which have entered into the molecule.

The chemical behaviour of many substances varies with the different classes of amines, and separation and purification of the amines formed in many of the methods above referred to may be carried out by making use of such differences. Primary and secondary amines usually give similar reactions, whilst tertiary amines are more stable, in accordance with the general rule for compounds which contain carbon atoms linked to the maximum possible number of hydrogen atoms.

Reactions.

1. *With nitrous acid.*

Primary amines, on boiling with potassium or sodium nitrite in acid solution, give alcohols or phenols with evolution of nitrogen.

$$RNH_2+HONO = ROH+N_2+H_2O.$$

Secondary amines give nitrosamines, which on boiling with conc. HCl are again transformed into the original amines.

$$RR'NH+HONO = RR'N\cdot NO+H_2O.$$
$$RR'N\cdot NO+2HCl = RR'NH\cdot HCl+NOCl.$$

Tertiary amines do not react.

Primary aromatic amino compounds react differently if their solutions are kept cooled. They give diazo- compounds according to the following equation:—

$$RNH_2,HCl+HONO = RN:NCl+2H_2O.$$

This reaction is of the greatest importance, for the diazo- compounds are very unstable, and on treatment with various substances either form substitution products of benzene hydrocarbons with evolution of nitrogen, or retain the nitrogen and form azo- compounds, which are the parent substances of the azo- dyes. Thus, if the diazo- compound be boiled with water, alcohol, cuprous chloride, bromide, or cyanide, phenol, benzene, chlor, brom, or cyan, derivatives respectively are produced. If the diazo- compound is treated with a substance containing a phenol or aromatic amino- group, a coloured substance is formed which is capable of fixing itself as a dye on a fabric. Compounds derived from unsubstituted amines have only a limited application for dyeing purposes, as they are generally insoluble in water; the sulphonic acids derived from them are, however, generally soluble, and are used extensively (*see* art. AZO-COLOURING MATTERS). The reactions are expressed by the following equations:—

$$C_6H_5N_2Cl+C_6H_5OH = C_6H_5N:NC_6H_4OH+HCl$$
$$C_6H_5N_2Cl+C_6H_5N(CH_3)_2 = C_6H_5N:NC_6H_4N(CH_3)_2+HCl$$

Tertiary aromatic compounds, such as dimethyl aniline, react with nitrous acid to form *p*-nitroso compounds, where the nitroso nitrogen is attached to the carbon of the benzene ring in the para-position to the substituted amino-group. These are highly coloured substances, and serve as intermediate compounds in the production of certain colouring matters (methylene blue, &c.), which are used in the colour industry. On treatment with caustic potash they give secondary amines and salts of nitroso phenol.

2. *With chlorides of aromatic sulphonic acids.*

Primary and secondary amines in strong alkaline solution are converted into amides by shaking with chlorides of aromatic sulphonic acids; of these amides, $Ph\cdot SO_2NHR$ and $PhSO_2NRR'$ respectively, the first only are soluble in dilute alkalis with formation of salts. Tertiary amines do not react. The primary and secondary amines can be regenerated from the amides by boiling with conc. HCl or H_2SO_4 at 120°–150° (Hinsberg, Ber. 23, 2963; Annalen, 1891, 265, 178).

3. *With acetyl chloride or acetic anhydride.*

Primary and secondary amines give, as a rule, acetyl derivatives which are insoluble in cold water; tertiary amines either do not react, or form soluble acetates and hydrochlorides. The primary and secondary amines may be regenerated by saponification of the acetyl derivatives. Since the velocity of the formation of the acetyl derivative of the primary is much greater than that of the secondary amine, a method based on this difference in property has been used to separate the two (Menschutkin, Chem. Zentr. 1900, 1, 1071; Potozki and Gwosdow, *ibid.* 1903, ii. 339).

The action of benzoyl chloride is similar to that of acetyl chloride.

4. *With oxalic esters.*

Several of the aliphatic primary and secondary amines react with ethyl oxalate, the former giving solid diamides and the latter liquid oxamic esters. Tertiary amines do not react. Primary and secondary amines are regenerated by boiling with potash (Hofmann, Ber. 1870, 3, 109, 776; Duvillier and Buisine, Ann. Chim. Phys. [5] 23, 299).

5. *With magnesium methyl iodides.*

Primary amines react, giving two molecules of methane for every molecule of amine:

$$RNH_2+2MeMgI = RN(MgI)_2+2CH_4.$$

Secondary amines react in a similar manner, but give one molecule of methane for every molecule of amine:

$$RR'NH+CH_3MgI = RR'NMgI+CH_4.$$

Tertiary amines either do not react or they form addition compounds with the reagent (Sudborough and Hibbert, Chem. Soc. Trans. 1909, 95, 477).

6. *With o-xylylene bromide.*

Primary amines react, giving two molecules of HBr and liquid derivatives of *o*-xylyleneimine (dihydro*iso*indol).

Secondary amines react, giving crystalline quaternary ammonium bromides and one molecule of HBr:

$$C_6H_4\langle^{CH_2Br}_{CH_2Br} + NH_2R = C_6H_4\langle^{CH_2}_{CH_2}\rangle NR + 2HBr$$

$$C_6H_4\langle^{CH_2Br}_{CH_2Br} + NHRR' = C_6H_4\langle^{CH_2}_{CH_2}\rangle N\langle^{R}_{R'} + HBr.$$

Br

Tertiary aliphatic amines give addition products of one molecule of xylylenebromide with two of amine. Tertiary aromatic amines and amino- compounds do not react (Scholtz, Ber. 1898, 31, 1707).

7. *With aromatic aldehydes.*

Primary and secondary amines form compounds with loss of water:

$$C_6H_5CHO + NH_2R = C_6H_5CHNR + H_2O.$$
$$C_6H_5CHO + 2NRR'H = C_6H_5CH(NRR')_2 + H_2O.$$

Tertiary amines do not react (Schiff, Annalen, 159, 159).

8. *With chloroform and potash.*

Primary amines give *iso*cyanides on warming.

$$RNH_2 + CHCl_3 + 3KOH = RNC + 3KCl + 3H_2O$$

(Hofmann, Ber. 3, 767).

Secondary and tertiary amines give no characteristic reaction.

9. *With carbon disulphide.*

Aliphatic primary and secondary amines react as follows:—

$$CS_2 + 2NH_2R = SC\langle^{NHR}_{SH\cdot NH_2R}.$$

$$CS_2 + 2NHRR' = SC\langle^{NRR'}_{SH\cdot NHRR'}.$$

On boiling the product of the action of CS_2 on primary amines with metallic salts ($HgCl_2$ or $FeCl_3$), mustard oils are produced, and primary amines partly regenerated.

$$SC\langle^{NHR}_{SH\cdot NH_2R} = SCNR + H_2S + NH_2R.$$

(Hofmann, Ber. 8, 105, 461; 14, 2754; 15, 1290).

Aromatic amines give substituted thioureas.

$$2RNH_2 + CS_2 = H_2S + (RNH)_2CS.$$

10. *With the alkali metals.*

Primary and secondary amines dissolve with evolution of hydrogen and formation of substances of the type $RNHK$ or RNK_2. Tertiary amines do not react.

11. *With oxidising agents.*

Oxidation with potassium permanganate decomposes aliphatic amines with formation of aldehydes and acids.

With Caro's acid (H_2SO_5), primary amines of the type RCH_2NH_2 are oxidised to hydroxylamines and hydroxamic acids, all of which give a characteristic colouration with ferric chloride. Ketoximes are formed from amines of the type $RR'CH\cdot NH_2$, whilst those of the type $RR'R''C\cdot NH_2$ give nitroso- and nitro- derivatives (Bamberger, Ber. 1902, 35, 4293; 1903, 36, 710).

With hydrogen peroxide aliphatic, secondary, and tertiary amines give hydroxylamines and N-oxides of type $RR'NOH$ and $RR'R''NO$ (Dunstan and Goulding, Chem. Soc. Trans. 75, 1104).

Oxidation of aniline and its para compounds gives quinone.

Diamines.

These may be regarded as derived from hydrocarbons by replacement of two hydrogen atoms by two amino- groups, or from two molecules of ammonia by replacement of two hydrogen atoms one from each molecule by a hydrocarbon residue. Certain of them occur as decomposition products of the animal organism, the chief of these being *putrescine* (tetramethylene diamine), and *cadaverine* (pentamethylene diamine). Diamino- acids are an important product of the decomposition of proteins.

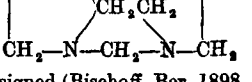
Preparation.—The methods are entirely analogous to those used in the preparation of monamines. Aliphatic diamines are obtained by the action of aqueous ammonia on dihalogen derivatives of hydrocarbons; this method is not generally applicable to the preparation of aromatic mono- or diamino- compounds, but a modification of it, which consists in treatment of *p*-chlormonamines with aqueous ammonia in presence of copper salts, is used in the commercial manufacture of *p*-phenylene diamine and its homologues (Ger. Pat. 204848, 1908). Aromatic diamino- compounds are prepared on the commercial scale chiefly by the reduction of dinitro- compounds; but practically all the methods for the production of monamines are also available for that of diamines.

Properties.—The aliphatic diamines are strongly basic substances, their basicity increasing with the number of methylene groups (Bredig, Zeitsch. physical. Chem. 1894, 13, 308). Their boiling-points are much higher than those of the corresponding monamines. Their hydroxides, which are diacid bases, are extremely stable, and are only decomposed on boiling with caustic alkalis or distillation over metallic sodium. The list of the chief aliphatic diamines and their physical constants (*see* p. 133) is taken from Meyer and Jacobsen's Lehrbuch der Organischer Chemie. The lower members of the aromatic diamino compound differ from the corresponding monamines by being easily soluble in water. Their solutions in water are easily oxidised, but the dry bases are stable in air.

Reactions.—Diamines give the ordinary reactions characteristic of the amino- group, but primary aromatic *o*-amino- compounds and to some extent aliphatic diamines, possess in addition, the property of forming condensation products containing nitrogen rings. *m*- and *p*-diamines do not exhibit this property.

1. *With aldehydes.*

With aliphatic diamines, cyclic compounds are formed as well as the ordinary alkylidene bases. Thus the action of formaldehyde on cold solutions of ethylene diamine results in the formation of a compound $C_8H_{16}N_4$, to which the formula

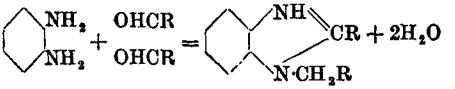


has been assigned (Bischoff, Ber. 1898, 31, 3254).

Aromatic *o*-diamino- compounds give aldehydines or anhydro bases:

Aliphatic Diamines.

	Formula	M.pt.	B.pt.	Sp.gr.
Ethylenediamine	$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	+8·5°	116·5°	0·902 (15°)
Propylene ,,	$CH_3{\cdot}CH(NH_2)CH_2{\cdot}NH_2$	—	119°–120°	0·878 (15°)
Trimethylenediamine	$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	—	135°–136° (738 mm.)	—
αβ-diaminobutane	$CH_3{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$	—	130°–155°	—
αγ- ,, ,,	$CH_3{\cdot}CH{\cdot}(NH_2){\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	—	141° (738 mm.)	—
αδ- ,, ,,	$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	27°–28°	158°–160°	—
βγ- ,, ,,	$CH_3CH(NH_2){\cdot}CH(NH_2){\cdot}CH_3$	only known	as its salts	—
αε- ,, pentane	$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	—	178°–179°	0·917 (0°)
βδ- ,, ,,	$CH_3CH(NH_2){\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_3$	α modification	46°–47° (20 mm.)	—
		β modification	43°–44° (11–12 mm.)	—
β-methyl-αδ-diaminobutane	$NH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	inactive form	172°–173°	0·8886 $\left(\frac{20°}{4°}\right)$
		active form	170°	—
αζ-diaminohexane	$NH_2{\cdot}CH_2(CH_2)_4CH_2{\cdot}NH_2$	39°–40°	100° (20 mm.)	—
βε- ,, ,,	$CH_3{\cdot}CH(NH_2)(CH_2)_2CH(NH_2)CH_3$	φ derivative	175·5° (753 mm.)	—
		x ,,	174·5°–175·5° (752 mm.)	—
β-methyl-αδ-diaminopentane	$NH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH(NH_2)CH_3$	—	175°	—
β-methyl-αε- ,, ,,	$NH_2{\cdot}CH_2{\cdot}CH{\cdot}(CH_3)(CH_2)_2CH_2{\cdot}NH_2$	—	78°–80° (13 mm.)	—
βγ-dimethyl-βγ-diaminobutane	$(CH_3)_2C(NH_2){\cdot}C(NH_2)(CH_3)_2$	97°–99°	147°–149° (740 mm.)	—
αη-diaminoheptane	$NH_2(CH_2)_7NH_2$	28°–29°	223°–225°	—
αθ-diaminooctane	$NH_2(CH_2)_8NH_2$	52°	225°–226°	—
βε-dimethyl-βε-diaminohexane	$(CH_3)_2C(NH_2)(CH_2)_2(NH_2)C(CH_3)_2$	solidifies at 0°	186° (758 mm.)	0·858 $\left(\frac{0°}{0°}\right)$
γδ-dimethyl-γδ-diaminohexane	$C_2H_5{\cdot}C(CH_3)(NH_2)(NH_2)C(CH_3){\cdot}C_2H_5$	only known	as its salts	—
αι-diaminononane	$NH_2(CH_2)_9NH_2$	37°–37·5°	258°–259°	—
βζ-dimethyl-βζ-diaminoheptane	$(CH_3)_2C(NH_2)(CH_2)_3(NH_2)C(CH_3)_2$	—	204°–206° (749 mm.)	0·8554 $\left(\frac{0°}{0°}\right)$
ακ-diaminodecane	$NH_2(CH_2)_{10}NH_2$	61·5°	140° (12 mm.)	—
βη-dimethyl-βη-diaminooctane	$(CH_3)_2C(NH_2)(CH_2)_4(NH_2)C(CH_3)_2$	31°	226°–229°	0·8344 $\left(\frac{28°}{0°}\right)$



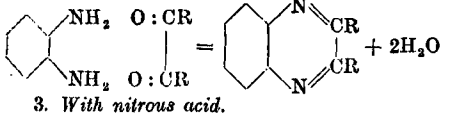
(Ladenburg and Engelbrecht, Ber. 1878, 11, 1653; Hinsberg, *ibid.* 1886, 19, 2025).

The aldehydines are strongly basic bodies, and not decomposed on boiling with dilute acids and alkalis. They are very stable towards oxidising and reducing agents. Their derivatives are used as dyes.

p- and *m*-diamines give alkylidene bases.

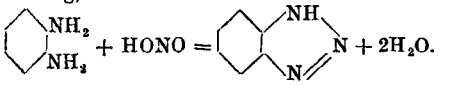
2. *With* 1.2-*dicarbonyl compounds* (*aldehydes or ketones*).

o-Diamino compounds react to give quinoxaline (azine) derivatives (Hinsberg, Annalen, 342, 1886):



3. *With nitrous acid.*

o-Diamino- compounds form azimines (Ladenburg)



Diamino- compounds both *m*- and *p*- will react in the ordinary way in presence of much hydrochloric acid, giving bis-diazo- compounds; in neutral solutions *m*-diamino- compounds give triamino azo benzene and its homologues. The reaction in the case of *m*-phenylene diamine is:

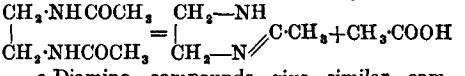
$$2C_6H_4(NH_2)_2 + HONO = NH_2{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_3(NH_2)_2.$$

The substances formed are brown and very deeply coloured. The reaction is used as a test for the presence of nitrites in water analysis (Griess, Ber. 1878, 11, 624).

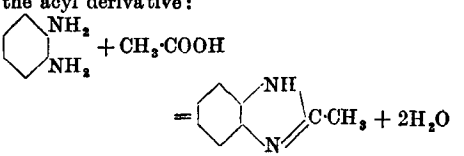
Aliphatic diamines give glycols and oxides.

4. *With organic acids, acid chlorides or anhydrides.*

Aliphatic diamines and *m*- and *p*-diamino- compounds form normal derivatives; in the cases of aliphatic substances, these derivatives are partially decomposed on heating, giving cyclic compounds of the iminoazole type:



o-Diamino- compounds give similar compounds, without the intermediate formation of the acyl derivative:



5. *With mineral acids.*

All diamines form stable salts. Those of

the aliphatic series are decomposed on heating with separation of ammonium salt and formation of cyclic compounds. Thus, tetramethylene diamine gives pyrrolidine and pentamethylene diamine gives piperidine:

$$NH_2(CH_2)_4NH_2,HCl = NH_4Cl + H_2C\begin{cases}CH_2\\CH_2\\NH\end{cases}CH_2$$

$$NH_2(CH_2)_5NH_2,HCl = NH_4Cl + H_2C\begin{cases}CH_2\\CH_2\\CH_2\\NH\end{cases}CH_2$$

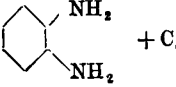
The higher homologues, however, do not form ring compounds containing a corresponding number of atoms in the ring. Thus, octomethylene diamine hydrochloride, on heating, does not give octomethylene imine, which would contain a ring of nine atoms, but 2-butylpyrrolidine. Similarly, decamethylene diamine gives 2-hexylpyrrolidine (Blaise and Houillon, Compt. rend. 1906, 142, 1541; 1906, 143, 361).

The aromatic diamines are the starting-points for the preparation of a large number of dyes, and hence are of commercial importance. The following are the chief members of the series:—

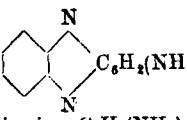
o-Phenylenediamine $C_6H_4(NH_2)_2$. First obtained by Griess by the distillation of *o-m-* and *m-p-* diaminobenzoic acid:

$$\underset{(1,\,2,\,3,\text{ or }1,\,3,\,4)}{C_6H_3(COOH)(NH_2)_2} = \underset{(1,\,2)}{C_6H_4(NH_2)_2} + CO_2$$

(J. pr. Chem. [2] 3, 143). By the reduction of *o*-nitraniline $C_2H_4(NO_2)(NH_2)$ (1, 2) (Zincke and Sintenis, Ber. 6, 123), or of *o*-dinitrobenzene $C_6H_4(NO_2)_2$ (1, 2) (Rinne and Zincke, Ber. 7, 1374), with tin and hydrochloric acid.—Crystallises from water in laminæ, melting at 102°. Boils at 252°. Readily soluble in water, alcohol, and ether. Diacid base, the sulphate $2[C_6H_4(NH_2)_2,H_2SO_4]\,3H_2O$ forms nacreous laminæ. It gives all the reactions for *o*-diamino-compounds referred to above. On oxidation with ferric chloride it gives a red compound, diaminophenazine:



$$+ C_6H_4(NH_2)_2 + 3O$$



$$= C_6H_2(NH_2)_2 + 3H_2O$$

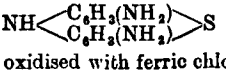
m-Phenylenediamine $C_6H_4(NH_2)_2$. By reducing *m*-dinitrobenzene or *m*-nitraniline with iron filings and acetic acid (Hofmann, Proc. Roy. Soc. 11, 518; 12, 639), or with tin and hydrochloric acid (Gerdemann, Zeitsch. f. Chem. 1865, 61). By reducing either (1, 2, 4)- or (1, 2, 6)-dinitrobenzoic acid with tin and hydrochloric acid, the carboxyl group being eliminated in the process (Zincke and Sintenis, Ber. 5, 791; Griess, Ber. 7, 1223). On a manufacturing scale it is prepared by reducing dinitrobenzene with iron turnings and hydrochloric acid.—Separates from its solutions as an oil which does not readily solidify unless brought in contact with a crystal of the base. Melts at 63°, and boils at 287°. Readily soluble in water. It gives the typical reactions of *m*-diamino- compounds (*see* above).

By the action of a diazobenzene salt on *m*-phenylenediamine, *chrysoïdine* (unsymmetrical diamidoazobenzene) is produced:

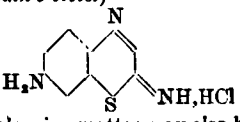
$$C_6H_5N_2Cl + C_6H_4(NH_2)_2 = HCl + C_6H_5N:N\cdot C_6H_3(NH_2)_2.$$

In the manufacture of phenylene-brown and chrysoïdine the solution of crude *m*-phenylenediamine hydrochloride obtained by the reduction of *m*-dinitrobenzene is employed, without first isolating the base. A violet colouring matter is obtained by heating *m*-phenylenediamine with aniline hydrochloride to 190°–200°, and a blue colouring matter by heating it with *m*-phenylenediamine hydrochloride (Krause, Ber. 9, 835).

p-Phenylenediamine $C_6H_4(NH_2)_2$. Obtained by reducing *p*-dinitrobenzene (Rinne and Zincke, Ber. 7, 871), or *p*-nitraniline (Hofmann, Proc. Roy. Soc. 12, 639), or aminoazobenzene (Martius and Griess, J. pr. Chem. 97, 263), with tin and hydrochloric acid, aniline being formed simultaneously in the case of aminoazobenzene. Along with diaminodiphenylamine by reducing aniline-black with tin and hydrochloric acid or with hydriodic acid and amorphous phosphorus (Nietzki, Ber. 11, 1097). By distilling (1, 2, 5)-diaminobenzoic acid (Griess, Ber. 5, 200). By action of *p*-chloraniline on aqueous ammonia in presence of copper salts. Crystals, melting at 147°. Boils at 267°. Sublimes in leaflets. Readily soluble in water, alcohol, and ether. Yields quinone on oxidation. When oxidised in the presence of primary amines or phenols it gives indamines and indophenols, these on heating produce safranines. By heating it with sulphur to 150°–180°, it is converted into diaminothiodiphenylamine (*leucothionine, Lauth's white*)



which, when oxidised with ferric chloride, yields thionine (*Lauth's violet*)



The latter colouring matter may also be obtained by the simultaneous oxidation of *p*-phenylenediamine and sulphuretted hydrogen by ferric chloride in aqueous solution (Lauth, Compt. rend. 82, 1441; Bull. Soc. Chim. 25, 422; Bernthsen, Annalen, 230, 108). If dimethyl-*p*-phenylenediamine $C_6H_4(NMe_2)(NH_2)$ is substituted for *p*-phenylenediamine in the foregoing reaction, tetramethylthionine (*methylene blue*) is formed (*v.* Methylene blue).

Tolylene-diamines (*Diaminotoluenes*) $C_6H_3(CH_3)(NH_2)_2$.

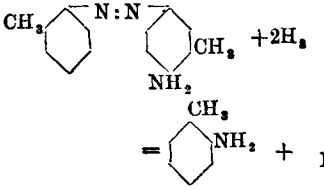
All the six possible compounds are known. Their physical constants are as follows:—

	M.pt.	B.pt.
1-Methyl-2 : 3-diaminobenzene	61°	255°
„ 2 : 4 „ „	99°	283°–285°
„ 2 : 5 „ „	64°	273°
„ 2 : 6 „ „	103°	—
„ 3 : 4 „ „	88°	265°
„ 3 : 5 „ „	—	284°

Only two of these, however, are of technical importance.

Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 4). Obtained by the reduction of the corresponding idnitrotoluene. Sparingly soluble in cold, readily soluble in boiling water, in alcohol, and in ether. Forms crystalline salts. As the two amino groups in this compound are in the meta- position to one another, it is an analogue of *m*-phenylenediamine, which it resembles in many of its reactions: thus 2:4-tolylenediamine may either wholly or in part replace the *m*-phenylenediamine used in the manufacture of phenylene-brown, producing colouring matters the shade of which is redder than that of ordinary phenylene-brown.

Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 5) is obtained by the reduction of the corresponding *m*-nitro-*o*-toluidine $C_6H_3(CH_3)(NH_2)(NO_2)$ (1,2,5) with tin and hydrochloric acid (Beilstein and Kuhlberg, Annalen, 158, 350; Ladenburg, Ber. 11, 1651). Formed along with *o*-toluidine when the aminoazotoluene prepared from *o*-toluidine is treated with the same reducing agent:



The two bases may be separated by fractional distillation (Nietzki, Ber. 10, 832). This reaction is utilised in preparing the mixture of *o*-toluidine and γ-tolylene-diamine which, after the addition of a second molecule of a monamine (either aniline or *o*- or *p*-toluidine), yields on oxidation safranine. On a large scale the aminoazotoluene is reduced with iron turnings and hydrochloric acid. Crystallises in colourless rosettes of tabular crystals. Readily soluble in water, alcohol, and ether, sparingly soluble in benzene. Yields on oxidation toluquinone $C_6H_3(CH_3)O_2$.

Other diamines of this series are—

Xylylene diamines:

1.3-dimethyl, 2.4-diaminobenzene, m.p. 64°.
1.3- „ 4.6 „ „ „ 104°.
1.3- „ 2.5 „ „ „ 77°.

Diaminotrimethylbenzenes: diamino- pseudocumenes:

1.2.4-trimethyl, 5.6-diaminobenzene, m.p. 90°.
1.2.4- „ 3.6 „ „ m.p. 78°.

Diamino mesitylene:

1.3.5-trimethyl, 2.4-diaminobenzene, m.p. 90°.

Similar diamines have been prepared from naphthalene and other hydrocarbons.

Triamines, Tetramines, and Pentamines.

Very few of these substances are known. Their properties are similar to those of other substances containing the amino group.

1.2.3-*triaminopropane*; b.p. 190° (Curtius, J. pr. Chem. 1900, 62, 232).

2.3.5-*triaminohexane* (Morelli and Marchetti, Atti del Accad. Lin. 1908, [5] 17, 1, 250).

The three modifications of triaminobenzene are all known.

1.2.3-*triaminobenzene*; m.p. 103°; b.p. 336°.

1.2.4-*triaminobenzene* is formed by reduction of *o*-*p*-dinitraniline or of chrysoidine. On oxidation it gives triaminophenazin.

1.3.5-*triaminobenzene* is only known in the form of its salts.

1.2.3.4. and 1.2.4.5-*tetraminobenzenes* prepared by the reduction of oximes and nitro compounds, have been isolated as their sparingly soluble sulphates (Nietzki and Schmidt, Ber. 1889, 22, 1648; Nietzki, Ber. 1887, 20, 2114).

Pentaminobenzene has been obtained as the hydrochloride with 3 molecules of HCl, by reduction of triaminodinitrobenzene (from tribrombenzene and ammonia). Pentaminotoluene has been similarly obtained.

Reduction of triaminotrinitrobenzene gives pentaminobenzene (Palmer and Jackson, Ber. 1888, 21, 1706; Palmer and Grindley, *ibid.* 1893, 26, 2304). M. B. T.

AMINO-ACIDS. The amino-acids may be conveniently described under the two headings (*a*) *Aliphatic Amino-acids*, and (*b*) *Aromatic Amino-acids*.

Aliphatic Amino-acids. The amino-fatty acids are of great physiological importance, many of them occurring in plant and animal organisms. They are products of proteid degradation, and may be obtained from proteins by heating with hydrochloric acid or baryta water. The general methods in use for preparing these acids are:

(i.) By treating the monohalogenated fatty acids with ammonia:

$$\underset{\text{Chloracetic acid.}}{CH_2Cl\cdot COOH} \rightarrow \underset{\text{Glycine.}}{CH_2(NH_2)COOH}.$$

(ii.) By heating the cyanhydrin of an aldehyde or ketone with ammonia and then hydrolysing the product, whereby an *a*-amino-acid is produced:

$$CH_3\cdot CH\langle^{CN}_{OH} \rightarrow CH_3\cdot CH\langle^{CN}_{NH_2} \rightarrow \underset{\text{Alanine.}}{CH_3\cdot CH(NH_2)CO_2H}.$$

(iii.) By the reduction of the cyanofatty acids with nascent hydrogen (Zn and HCl or by heating with HI)

$$\underset{\text{Cyanoformic acid.}}{CN\cdot CO\cdot OH} + 2H_2 = CH_2(NH_2)CO_2H.$$

The amino-fatty acids are crystalline bodies with usually a sweet taste, and are readily soluble in water. They are amphoteric, *i.e.* feeble bases and feeble acids. Important members are glycine, alanine, phenylalanine, tyrosine, leucine, and valine, serine, cystine, tryptophane, histidine, arginine, lysine, aspartic acid, and glutaminic acid, which are described under their respective headings (*v.* also Proteins).

(*b*) **Aromatic Amino-acids.** A true aromatic amino-acid such as anthranilic acid, contains both the amino and the carboxyl- groups united to carbon atoms in the benzene ring. Isomeric with these are acids which contain the amino group or the carboxyl- group or both, introduced into fatty side chains, the last two classes being really substituted fatty acids.

The general methods in use for preparing aromatic amino-acids are:

(i.) By reducing the corresponding nitro-acids:

$$\underset{\text{o-nitrobenzoic acid.}}{C_6H_4(NO_2)COOH(1:2)} \rightarrow \underset{\text{Anthranilic acid.}}{C_6H_4(NH_2)COOH(1:2)}$$

(ii.) By treating the halogen esters with

potassium phtalimide and hydrolysing the product with hydrochloric acid at 200°.

The aromatic amino-acids are used in the preparation of azo-dyestuffs (*q.v.*).

o-Aminobenzoic acid. Anthranilic acid

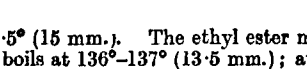
$C_6H_4(NH_2)CO_2H$ (1 : 2).

It was first obtained by heating indigo with caustic potash (Fritzsche, Annalen, 39, 83). It may be prepared by the reduction of *o*-nitrobenzoic acid with tin and hydrochloric acid (Beilstein and Kühlberg, Annalen, 163, 138), or with zinc and sodium bisulphite (Goldberger, Chem. Zentr. 1900, ii. 1014; *v.* also Preuss and Binz, Zeit. angew. Chem. 1900, [16] 385 and Bad. Anil. u. Soda Fab. Eng. Pat. 18319; J. Soc. Chem. Ind. 1900, 774); by heating *o*-chlorbenzoic acid and ammonia at 125° under pressure (Fabw. Meister, Lucius und Brüning, D. R. P. 145604; Chem. Soc. Abst. 1904, i. 50); by treating phthalimide with bromine and caustic potash (Hoogewerff and van Dorp, Ber. 1891, Ref. 966; Bad. Anil, und Soda Fab. D. R. P. 55988; Frdl. ii. 546; Amsterdamsche Chininefabrik. Eng. Pat. 18246; J. Soc. Chem. Ind. 1891, 831); by boiling phthalhydroxylamic acid, formed by treating phthalic anhydride with hydroxylamine, with caustic soda or sodium carbonate (Cie. Par. de Coul. d'Aniline, Fr. Pat. 318050; J. Soc. Chem. Ind. 1902, 1392; Farbw. Meister, Lucius und Brüning, Eng. Pat. 1982, D. R. P. 136788; Basler Chemische Fabw.; D. R. PP. 130301, 130302); by reducing sulphanthanilic acid electrolytically or with sodium amalgam (Kalle and Co. D. R. P. 129165; Chem. Zentr. 1902, i. 1138; D. R. P. 146716; Chem. Soc. Abst. 1904, i. 159); by treating *o*-nitrotoluene with concentrated alcoholic or aqueous alkali (Bad. Anil. und Soda Fab. D. R. P. 114839; Chem. Zentr. 1900, ii. 1892); and by heating isatoic acid with concentrated hydrochloric acid (Kolbe, J. pr. Chem. [2] 30, 124).

Anthranilic acid is of great commercial importance, as it is one of the intermediate products in the manufacture of synthetical indigo. It crystallises in colourless plates, m.p. 145°, and is readily soluble in alcohol or water. It condenses with formaldehyde, forming compounds which are of use in the preparation of indigo (Heller and Fiesselmann, Annalen, 324, 118; Bad. Anil. und Soda Fab. D. R. PP. 117924, 158090, 158346; J. Soc. Chem. Ind. 1905, 615). Reduction with sodium amalgam in hydrochloric acid solution yields *o*-aminobenzylalcohol (Langguth, Ber. 1905, 2062). Concentrated hydriodic acid decomposes it at 200° into ammonia, carbon dioxide, aniline and benzoic acid (Kwisda, Monatsh. 12, 427); whilst nitrous acid converts it in aqueous solution into salicylic acid. Anthranilic acid is employed in the preparation of azo- dyestuffs (*q.v.*) (*v.* also Bayer and Co. D. R. PP. 58271, 60494, 60500, 86314; Frdl. iii. 614, *et seq.* iv. 795).

The methyl ester of anthranilic acid occurs in Neroli oil (oil of orange flowers) (Walbaüm, J. pr. Chem. 1899, 59, [6–7] 350). It is prepared by heating anthranilic acid with methyl alcohol and hydrochloric acid (Erdmann, Ber. 1899, 1213; D. R. P. 110386) or from acetylanthranilic acid, methyl alcohol and mineral acids (Erdmann, D. R. P. 113942; Chem. Zentr. 1900, ii. 831). It is a crystalline solid, m.p. 24·5°, b.p. 135·5° (15 mm.). The ethyl ester melts at 13° and boils at 136°–137° (13·5 mm.); at 266°–268° (corr.) (Frankel and Spiro, Ber. 1895, 1684). Aminobenzoic acid alkamine esters (*v. p*-aminobenzoic acid).

Anthranil



is the anhydride or lactam of anthranilic acid, its constitution being still under discussion. It is prepared by treating the dimercury derivative of *o*-nitrotoluene (obtained by suspending *o*-nitrotoluene in water and heating it with freshly precipitated mercuric oxide and caustic soda) with concentrated hydrochloric acid and decomposing the product with water (Kalle and Co. Fr. Pat. 370522; D. R. P. 194364; J. Soc. Chem. Ind. 1907, 278; 1908, 713); by heating *o*-nitrotoluene with caustic soda to 170° (Kalle and Co. D. R. P. 194811; Chem. Soc. Abstr. 1908, i. 786); by the reduction of *o*-nitrobenzaldehyde with aluminium amalgam (Brühl, Ber. 1903, 3634); and by the oxidation of *o*-aminobenzaldehyde with a neutral solution of Caro's persulphuric acid (Bamberger and Demuth, Ber. 1903, 829; 2042).

Anthranil is an oil, readily volatile in steam, possesses a peculiar odour, and boils at 210°–213°. It dissolves in alkalis to form salts of anthranilic acid and on treatment with acetic anhydride yields acetylanthranilic acid.

m-Aminobenzoic acid. Benzamic acid $C_6H_4(NH_2)CO_2H$ (1 : 3), is prepared by reducing *m*-nitrobenzoic acid with ammonium sulphide and subsequently precipitating the acid with tartaric acid (Holleman, Rec. Trav. Chim. 1902, [ii.] 21, 56; *v.* also Gerland, Annalen, 91, 188). It is a colourless crystalline solid, m.p. 174°; sparingly soluble in cold, readily so in hot water. Reduction with sodium amalgam in hydrochloric acid yields *m*-aminobenzyl alcohol (Langguth, Ber. 1905, 2062). Concentrated hydriodic acid transforms it into ammonia and benzoic acid (Kwisda, Monatsh. 12, 428). *m*-Aminobenzoic acid is used in the preparation of azo-dyestuffs (*q.v.*) (Bayer and Co., D. R. PP. 58271, 59081, 60494, 60500, 63104, 64529, 69445, 74198, 74516, 78493, 86314; Frdl. iii. 614 *et seq.*, 777 *et seq.*; iv. 793, 795; Ges. f. Chem. Ind., D. R. P. 76127; Frdl. iii. 746). Aminobenzoic acid alkamine esters (*v. p*-aminobenzoic acid).

p-Aminobenzoic acid $C_6H_4(NH_2)CO_2H$ (1 : 4), is prepared by the reduction of *p*-nitrobenzoic acid with ammonium sulphide (Fischer, Annalen, 127, 142) or with tin and hydrochloric acid (Beilstein and Wilbrand, Annalen, 128, 164). It is a colourless crystalline solid, m.p. 186°–187°, readily soluble in water, alcohol, or ether. Strong hydrochloric acid at 180° converts it into aniline and carbon dioxide (Weith, Ber. 1879, 105) and hydriodic acid at 200° into ammonia, carbon dioxide, and benzoic acid (Kwisda, Monatsh. 12, 428). *p*-Aminobenzoic acid is used in the preparation of azo- dyestuffs (*q.v.*) (Bayer and Co. D. R. PP. 58271, 60494, 60500, 86314; Frdl. iii. 614 *et seq.*; iv. 795; Ges. f. Chem. Ind., D. R. P. 76127; Frdl. iii. 746).

Many complicated alkyl- and alkamine esters of the aminobenzoic acids have been prepared and they are claimed to be valuable anæsthetics,

(Farbw. Meister, Lucius, and Bruning, D. R. PP. 170587, 172301, 172447, 172568, 179627, 180291, 180292, 194748, Eng. Pat. 17162, Fr. Pat. 361734, U. S. Pat. 812554; J. Soc. Chem. Ind. 1906, 607; 1907, 434; Chem. Soc. Abstr. 1906, i. 845 *et seq.*; 1907, i. 923; 1908, i. 638; Merck, D. R. P. 189335; J. Soc. Chem. Ind., 1908, 471; Bayer and Co. D. R. PP. 211801, 218389, Eng. Pat. 4321; J. Soc. Chem. Ind. 1909, 854; Chem. Zentr. 1910, i. 782; Fritzsche, Eng. Pat. 2020, Fr. Pat. 398259, D. R. P. 213459; J. Soc. Chem. Ind. 1909, 814).

4-Amino-o-toluic acid $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 4 : 2); m.p. 196°. Obtained by the reduction of 4-nitrotoluic acid with tin and hydrochloric acid (Jacobsen and Wierss, Ber. 1883, 1959).

5-Amino-o-toluic acid $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 5 : 2); m.p. 153°, is obtained by the reduction of 5-nitrotoluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1884, 164).

6-Amino-o-toluic acid $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 6 : 2). Method of preparation as above; m.p. 191° (J. and W. *l.c.*).

2-Amino-m-toluic acid $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 2 : 3). Method of preparation as above; m.p. 132° (Jacobsen, Ber. 1881, 2354), 172° (Jürgens, Ber. 1907 4409).

4-Amino-m-toluic acid (*Methylanthranilic acid*) $C_6H_3 \cdot CH_3(NH_2) \cdot CO_2H$ (1 : 4 : 3). Obtained by reduction of 4-nitro-*m*-toluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1881, 2354) or by treating *p*-methylisatoic acid with concentrated hydrochloric acid (Panaotovic, J. pr. Chem. [2] 33, 62); m.p. 172° (Ehrlich, Ber. 1901, 3366), 175° (Findeklee, Ber. 1905, 3533).

6-Amino-m-toluic acid $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 6 : 3); m.p. 167°. Obtained by reduction of 6-nitro-*m*-toluic acid (Beilstein and Kreusler, Annalen, 144, 147).

2-Amino-p-toluic acid $C_6H_3 \cdot CH_2 \cdot (NH_2) \cdot CO_2H$ (1 : 2 : 4); m.p. 164°–165°. Method of preparation as above (Ahrens, Zeitsch. f. Chemie, 1869, 104).

3-Amino-p-toluic acid (*Homo-anthranilic acid*) $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 3 : 4); m.p. 177°. Method of preparation as above (Niementowski and Rozanski, Ber. 1888, 1997; Noyes, Amer. Chem. J. 10, 479).

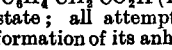
1'-Amino-o-toluic acid (*Benzylamine-o-carboxylic acid*) $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ (1 : 2). Obtained by digesting 1 part of *o*-cyanobenzylphthalimide with 4 parts of concentrated sulphuric acid (Gabriel, Ber. 1887, 2231). Crystalline non-volatile solid.

1'-Amino-m-toluic acid (*Benzylamine-m-carboxylic acid* $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ (1 : 3); m.p. 215°–218°. By heating at 200° a mixture of 2 grams *m*-cyanobenzylphthalimide and 10 c.c. concentrated hydrochloric acid (Reinglass, Ber. 1891, 2419).

1'-Amino-p-toluic acid (*Benzylamine-p-carboxylic acid*) $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ (1 : 4). Method of preparation as above (Günther, Ber. 1890, 1060). Crystalline solid.

2-Amino-α-toluic acid (*2-Aminophenylacetic acid*) $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ (1 : 2) is not known in the free state; all attempts to prepare it result in the formation of its anhydride, oxindole.

Oxindole



is obtained by treating 2-nitro-α-toluic acid with tin and hydrochloric acid (Bayer, Ber. 1878, 583), or by reducing dioxindole with tin and hydrochloric acid, or with sodium amalgam (Bayer and Knop, Annalen, 140, 29). Crystallises in colourless needles; m.p. 120°.

3-Amino-α-toluic acid (*3-Aminophenylacetic acid*) $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ (1 : 3). Obtained by reducing 3.nitro-α-toluic acid with tin and hydrochloric acid; m.p. 148°–149° (Gabriel and Borgmann, Ber. 1883, 2065).

4-Amino-α-toluic acid (*4-Aminophenylacetic acid*) $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ (1 : 4). Method of preparation as above (Radziozewski, Ber. 1869, 209); m.p. 199°–200° (Bedson, Chem. Soc. Trans. 1880, 92).

α-Aminophenylacetic acid $C_6H_5 \cdot CH(NH_2)CO_2H$. Obtained by heating α-phenylbromacetic acid with aqueous ammonia at 100°–110° (Stöckenius, Ber. 1878, 2002); m.p. 256° (Tiemann, Ber. 1880, 383). Sublimes without melting at 265° (Elbers, Annalen, 227, 344).

α-AMINO CAPROIC ACID *v.* LEUCINE.

AMINONAPHTHOPHENAZINE *v.* AZINES.

AMINOPHENYLACETIC ACID *v.* AMINO-ACIDS (AROMATIC).

AMINOPHENOPHENANTHRAZINE *v.* AZINES.

α- and β-AMINOPROPIONIC ACIDS *v.* ALANINE.

α-AMINO-*iso*-VALERIC ACID *v.* VALINE.

AMLA (Beng.), **AMLIKA** (Hind.), **AMLIKU** (Ass.), **OWLA** (Mechi), **NELLI** and **TOPPINELLI** (Tam.). A euphorbiaceous Indian tree, *Phyllanthus emblica* (Linn.), the fruits of which (*Emblic myrobalans*) are used in a fresh condition as a laxative, and, when dried, as an astringent (Dymock, Pharm. J. [3] 10, 382). The fruits are also pickled and eaten, and used for tanning and dyeing.

AMMONAL *v.* EXPLOSIVES.

AMMONIA. *Volatile alkali, alkaline air, spirit of hartshorn.* Solutions of ammonia have been known from very early times, but the substance itself was first clearly recognised by Priestley, who obtained it by heating the aqueous solution and collecting the gas, which he termed *alkaline air*, over mercury. Scheele proved that it contained nitrogen; and Berthollet, and more accurately Austin, demonstrated its real nature, and determined the proportions of its constituents.

Ammonia (or its salts) is found in small quantities in the air, and in most natural water; in the juice of plants, in most animal fluids, in many soils, and in a few minerals, ochres, clays, marls, &c. Ammonia can be obtained synthetically in small quantity by the passage of electrical discharges through a mixture of nitrogen and hydrogen (Donkin, Pogg. Ann. 21, 281); or as nitrite by the action of a strong induction spark on a mixture of nitrogen and water vapour (Thénard, Compt. rend. 76, 983); or as chloride by sparking a mixture of hydrogen, nitrogen, and hydrogen chloride (Deville, Compt. rend. 60, 317); or by the action of heated spongy platinum, pumice, &c., on a mixture of hydrogen and nitric acid.

For laboratory purposes the gas is usually prepared by heating a mixture of ammonium chloride or sulphate with slaked lime, or by gently warming the concentrated solution, and drying the gas over quicklime. (For the preparation of the chemically pure gas, *see* Stas, Zeitsch. anal. Chem. 6, 423.)

Ammonia is a colourless gas, having a very pungent characteristic smell, and is poisonous when breathed in quantity, destroying the mucous membrane. It has a sp.gr. of 0·5967 (air = 1), 1 litre of the gas at 0° and 760 mm. weighing 0·7708 gram, and readily liquefies on compression, the critical temperature being 131°, and the critical pressure 113 atm. Liquid ammonia is colourless and very mobile, and has a sp.gr. at 0°/4° of 0·6385 (Dieterici), 0·6388 (Drewes), the coefficient of expansion being very high and increasing rapidly with the temperature. It boils under atmospheric pressure at −33·5°, and freezes to a white crystalline solid at −75° (Faraday), −77° (Brill), the vapour pressure being as follows (Regnault, J. 1863, 70) :—

at −30°	1·14 atm.	at 0°	4·19 atm.
„ −20°	1·83 „	„ 10°	6·02 „
„ −10°	2·82 „	„ 20°	8·41 „

Its latent heat of evaporation is, with the exception of that of water, higher than that of any known liquid, amounting to about 5000 cal. at 15° and 5600 cal. at its boiling-point, and on this account it is produced commercially in large quantity for employment in freezing machines. In many of its physical properties the liquid resembles water, and it acts as a solvent for a large number of substances.

Ammonia gas burns with difficulty in the air when cold, but inflames more readily on heating, and still more readily in oxygen, giving a greenish-yellow flame of high temperature. In presence of suitable catalysts, such as copper, iron, nickel, and especially platinum, ammonia is oxidised by oxygen at lower temperatures with production of oxides of nitrogen, the manufacture of nitric acid from ammonia by Ostwald's process (Eng. Pat. 698, 1902) being carried out in this manner. A number of the elements, when heated in ammonia gas, yield corresponding nitrides, boron, magnesium; and titanium being especially active in this respect, whilst the alkali metals give rise to amides. With carbon at temperatures above 750° ammonia is partly dissociated, and partly converted into hydrocyanic acid, the presence of the latter in crude coal gas being largely due to this reaction.

Many salts combine with ammonia to form stable compounds at the ordinary temperature, the ammonia playing the same part as water of crystallisation. It is evolved on heating, liquid ammonia having been first obtained by Faraday, in 1823, by warming the compound with silver chloride $2AgCl,3NH_3$, in a sealed tube.

The action of heat upon ammonia has been investigated by Ramsay and Young (Chem. Soc. Trans. 45, 92), Perman (Proc. Roy. Soc. 74, 110; 76A, 167), Haber and v. Oordt (Zeitsch. anorg. Chem. 44, 341), and Nernst and Jost (Zeitsch. Elek. 13, 521). Under atmospheric pressure, decomposition commences at temperatures below 500°, its extent increasing rapidly with the temperature, but the speed with which equilibrium is attained between undecomposed ammonia and nitrogen and hydrogen varies greatly according to the nature of the surfaces with which the gases are in contact. Glass is very inactive, but porcelain and many metals and their oxides have a very strong accelerating effect. In presence of the latter decomposition becomes nearly complete at 630° under atmospheric pressure, but the last traces do not disappear even at 1000°. Conversely, in presence of iron as catalyst, Haber and v. Oordt find that at 1000° traces of ammonia are formed from nitrogen and hydrogen at atmospheric pressure, and Nernst and Jost have found that small quantities are formed at the same temperature under the greater pressure of 50–70 atm. Recently, however, Haber has found that at temperatures of 500°–550° under 200 atm. pressure, in presence of metallic osmium or uranium, nitrogen and hydrogen combine to a considerable extent (*see* below).

Ammonia gas is very soluble in water, alcohol, ether, and many saline solutions, the aqueous solution (caustic ammonia or *liquor ammoniæ*) being of great commercial importance. One gram of water at 0° and 760 mm. absorbs 1148 c.c. or 0·875 gram of ammonia, at 10° 0·679 gram, at 20° 0·526 gram, at 30° 0·403 gram, and at 100° 0·074 gram (Roscoe and Dittmar, Chem. Soc. Trans. 12, 128; Sims, Chem. Soc. Trans. 14, 1; see also Perman, Chem. Soc. Trans. 79, 718; 83, 1168). In the act of solution much heat is evolved, and according to Thomsen, NH_3+aq. = 8430 cals.

The density of aqueous solutions of ammonia of varying strength, according to the determinations of Lunge and Wiernik, is given on p. 139.

The solution is very strongly alkaline, and unites with acids to form the ammonium salts, and it is frequently supposed that the solution contains ammonium hydroxide $NH_4{\cdot}OH$, corresponding to NaOH and KOH. The evidence for this view is not altogether conclusive, and the physical properties of the solution at the ordinary temperature are in some respects opposed to the presence of the compound NH_4OH, and in favour of the supposition that the ammonia is dissolved as such. At very low temperatures, however, Rupert (J. Amer. Chem. Soc. 31, 866; 32, 748) has shown that two definite hydrates exist, the freezing-point curve of mixtures of ammonia and water in varying proportions showing two well-defined minima at −87° and −94° respectively, the composition at these two points corresponding to the formulæ NH_3,H_2O and $2NH_3,H_2O$. The first-named forms small colourless crystals resembling those of sodium and potassium hydroxide; and the latter, larger needle-shaped crystals. Whether these are true hydrates or are to be regarded as ammonium hydroxide NH_4OH and ammonium oxide $(NH_4)_2O$, is at present uncertain.

The aqueous solution of ammonia also dissolves many metallic oxides and hydroxides, such as $Ag_2O,Cu(OH)_2$, as well as many salts which are insoluble in water, such as silver chloride and phosphate, and cuprous chloride, and also acts as a solvent for many fats and resins. The solution of cupric hydroxide in ammonia is of considerable commercial importance, as it is a solvent for cellulose, and is used in large quantities in the manufacture of artificial silk.

I. Technical sources of ammonia.[1] Ammonia is formed in nature chiefly during the decay of nitrogenous organic substances, and conse-

[1] For more complete details, *see* Lunge's Coal-Tar and Ammonia, chaps. xii.–xv. (Gurney and Jackson, 1909).

quently exists in considerable quantity both in the soil and the atmosphere. Whilst this is of the greatest importance for agriculture, it is only possible in very exceptional cases to utilise this source for the manufacture of ammonium salts, practically the whole of the world's production being obtained by the destructive distillation of nitrogenous organic matter, chiefly coal.

A. *Natural occurrence of ammoniacal compounds in quantity of commercial importance.*—Ammonium carbonate has been found in guano deposits on the West Coast of South America, and has been imported into Europe, a sample imported into Germany in 1848 consisting essentially of ammonium bicarbonate mixed with some insoluble matter. Ammonium sulphate is contained in the Tuscan 'soffioni,' and is there obtained in considerable quantity as a by-product in the manufacture of boric acid. Ammonium chloride, together with sulphate, is sometimes found in the neighbourhood of volcanoes.

B. *Synthetic processes for production of ammonia.*—Very many attempts have been made to effect the manufacture of ammonia from atmospheric nitrogen, and a large number of processes with this object have been patented. Hitherto, however, no method which has been proposed has proved successful on a commercial scale, for although, as stated above, nitrogen and hydrogen combine together to a slight extent to form ammonia, when heated together under suitable conditions, the yield at high temperatures is so small that the cost of production would be prohibitive. With many of the methods proposed—such as those of Swindells (Eng. Pat. June 21, 1876), Rickman (Eng. Pat. 3341, 1878), Glover (Eng. Pat. 1890, 1880), Solvay (Bull. Soc. chim. 25, 527), Wagner (Jahresbericht. 1876, 444), Bassett (Eng. Pat. 4338, 1879)—it is very doubtful whether, in fact, any ammonia is produced synthetically, the ammonia obtained being more probably all derived from the nitrogen present in the coal or coke employed in each of these processes. The processes of Johnson (Chem. News, 43, pp. 42, 288), Woltereck (J. Soc. Chem. Ind. 1908, 158, 978; Eng. Pat. 2461, 1902; 16,504, 1904; 8358, 1905), Mond (J. Soc. Chem. Ind. 1889, 505), and Roth (D. R. P. 191914), in which a mixture of nitrogen and hydrogen is passed over various heated catalytic agents, do not appear to have resulted in any commercial yield of ammonia. Haber (Zeitsch. Elek. Chem. 16, 244) has found that when a mixture of 1 vol. of nitrogen and 3 vols. of hydrogen is heated with metallic osmium to 550° under a pressure of 200 atm., a very considerable production of ammonia takes place amounting to 8 p.c. of the mixed gas, and although osmium is too scarce and expensive for technical use, it may be replaced by metallic uranium with good results. With a small apparatus constructed to allow of the circulation of the mixed gas under this pressure over uranium heated to

DENSITY OF AQUEOUS SOLUTIONS OF AMMONIA AT 15° (LUNGE AND WIERNIK).

Sp.gr.	NH_3 p.c.	1 litre contains NH_3 g.	Correction of sp.gr. for ± 1°	Sp.gr.	NH_3 p.c.	1 litre contains NH_3 g.	Correction of sp.gr. for ± 1°
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

about 500°, and cooling between each passage of the gas over the metal, Haber has synthesised ammonia at the rate of about 90 grams per hour, the ammonia separating out on cooling under these conditions as a liquid. Larger plant is now being erected by the Badische Anilin und Sodafabrik.

Attempts to effect the synthesis by the passage of the silent discharge and of sparks through the mixture of nitrogen and hydrogen have also failed to effect a sufficient yield of ammonia. Patents for this type of process have been taken out by Young (Eng. Pat. 1700, 1880), Müller and Geisenberger (Eng. Pat. 1481, 1879; 1592, 1879), the Société d'Azote (D. R. P. 17070), Nithack (D. R. P. 95532), West-Deutsche Thomasphosphatwerke (D. R. P. 157287 and 179300), Gorianoff (Fr. Pat. 368585), Hooper (U.S. Pat. 791194), and Cassel (D. R. P. 175480); see also Briner and Mettler (Compt. rend. 144, 694), and Davies (Zeitsch. physikal. Chem. 64, 657). A similar lack of commercial success has hitherto attended the efforts to produce ammonia by combining atmospheric nitrogen with elements which readily form nitrides, such as boron, titanium, magnesium, and calcium, and subsequent conversion of the nitride into ammonia by the action of steam; patents in this respect having been taken out by Bassett (Eng. Pat. 4338, 1897), Lyons and Broadwell (U.S. Pat. 816928), Wilson (Eng. Pat. 21755, 1895), Mehner (Eng. Pat. 12471, 1895; 2654, 1897; 28667, 1903), Kaiser (Eng. Pat. 26803, 1905), Borchers and Beck (D. R. P. 196323), and Roth (D. R. P. 197393).

C. *Production from cyanides.*—It has long been known that nitrogen combines at high temperatures with carbon and alkalis with production of cyanides, and many attempts have been made during the last fifty years to manufacture cyanides in this manner and to convert these subsequently into ammonia by the action of superheated steam. The large demand for cyanides themselves, resulting from their employment in the extractions of gold from the mine tailings, and the fact that at present nitrogen, in the form of cyanide, commands a higher price than in the form of ammonia, has made such processes of no value for ammonia production under existing conditions, and in fact, at the present time, the opposite process of converting ammonia into cyanides is carried on to a large extent. The methods proposed, so far as they relate to cyanide production, will be discussed under that heading, but one method may be here mentioned, namely, the manufacture of calcium cyanamide, $Ca:N\cdot C \vdots N$, according to Frank and Caro's process (J. Soc. Chem. Ind. 1908, 1093), by the action of nitrogen on heated calcium carbide, this being simultaneously a cyanogen and an ammonia derivative (*v. Cyanamide*, art. NITROGEN, ATMOSPHERIC, UTILISATION OF). This substance may readily be converted into ammonia by the action of superheated steam, but it is for the most part directly employed on the land as a nitrogenous manure.

D. *Ammonia from urine, sewage, and animal excreta.*—Urine is not merely the oldest, but for centuries was the only source for obtaining ammonia compounds on a commercial scale. It is stated that sal-ammoniac made from it was an article of commerce as early as 1410, and that the Jesuit Sicard in 1720 saw the manufacture of it in the Delta of the Nile. In Egypt sal-ammoniac was made by burning camels' dung and collecting the sublimate. Putrefied urine (in which the urea has passed into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes. The methodical working up of urine collected in large quantities, or of sewage for obtaining ammonia therefrom, has been carried out in the neighbourhood of some large towns, *e.g.* Paris, but only a very small quantity of ammonia in comparison with the enormous quantity excreted is actually obtained in this way.

Normal urine contains per litre from 20 to 35 grams urea (carbamide), which after a short time is changed into ammonium carbonate under the influence of a micro-organism. An adult man produces from 22 to 37 grams urea per 24 hours, together with a little uric acid, corresponding to 12·5–21 grams NH_3 per day, or between 9 and 17 lbs. per annum. If all the ammonia obtainable from London urine were recovered this would amount to 100,000 tons of ammonium sulphate per annum.

Owing to the now almost universal adoption of the removal of sewage by means of water, the dilution of the ammonia in the combined sewage is so great that its recovery is hardly practicable, but with concentrated pan sewage, recovery of ammonia is carried on in a few places, especially in Paris. A large number of patents have been taken out for the recovery of ammonia both from sewage and also from the more concentrated sludge deposited in the collecting tanks at the sewage works, among which may be mentioned Duncan (D. R. PP. 27148, 28436), Young (Eng. Pat. 3562, 1882), Bolton and Wanklyn (Eng. Pat. 5173, 1880), Gesellschaft für Wasserabklärung, Berlin (D. R. P. 161166), Butterfield and Watson (Eng. Pat. 19502, 1905), Taylor and Walker (U.S. Pat. 603668).

In Paris there are daily 2200 cubic metres (say tons) of urine and night soil taken out of the fosses, and treated by various processes. In the Bilange process the sewage is mixed with milk of lime and allowed to settle, the liquid portion is worked for ammonia, the muddy deposit (containing a great many albuminoid matters) is heated by steam, passed through filter-presses and sold as manure. In the Kuentz process the muddy deposit is mixed with a reagent prepared by treating a mixture of bauxite, natural phosphate of lime, and hydrated oxide of iron with hydrochloric acid. The resulting mass is passed through filter-presses; the cakes remaining in these contain all the phosphoric acid (10–12 p.c.) as dicalcic phosphate, precipitated by ammonium carbonates; the iron has absorbed the sulphur compounds, and the alumina has modified the albuminous and slimy matters which would have impeded the filtration. The percentage of nitrogen in these cases is 3–3·5.

Ketjen (Zeitsch. angew. Chem. 1891, 294) also reports a successful recovery of ammonia from concentrated sewage by distillation with lime at Amsterdam.

E. *Ammonia from guano, &c.*—Whilst the ammonia obtainable from excreta is mostly lost for immediate recovery, as it quickly passes away into the water, the soil, or the air, there are a few exceptions to this rule presented by the deposits of birds' excrements on some desert islands, and a few similar cases. In this 'guano,' ammonia salts exist already preformed, and ammonia can be formed from other nitrogenous substances contained therein by heating guano with lime (as patented by Young in 1841), but this process is not remunerative, since the direct manurial value of guano is much superior to that of the ammonia salts obtainable therefrom.

F. *Manufacture of ammonia by the destructive distillation of nitrogenous organic matter.*—The total quantity of ammonia commercially produced by all of the methods described above is at present almost negligible, nearly the whole of the world's supply of ammonia and its salts being obtained as a by-product in the course of other manufactures in which nitrogenous organic matter is subjected to the process of destructive distillation. By far the greatest proportion is obtained in the manufacture of illuminating gas, power gas, or coke from coal, and in the distillation of shale for the production of shale oil. A considerable amount is also recovered from the gases evolved from blast-furnaces where coal is used as fuel, and smaller quantities from the distillations of bones, horn, and other animal refuse, and also from the residue obtained from beet-root molasses.

The total production of ammonia in the United Kingdom, calculated as sulphate, for the years 1907–8–9, is shown in the following table, the figures for 1889 being also given to indicate the increase in production during the past 20 years. The statistics are taken from the Annual Reports of the Chief Alkali Inspector :—

	1889	1907	1908	1909
Gas works	87,000	165,474	165,218	164,276
Iron works	5,500	21,024	18,131	20,228
Shale works	22,000	51,338	53,628	57,048
Coke ovens	—	53,572	64,227	82,886
Producer gas and other carbonising works	3,000	21,873	24,024	24,705
	117,500	313,281	325,228	349,143

The world's production for 1907 is given in Mineral Industry, 16, 31, as follows :—

Great Britain	331,220	metric tons (2204 lbs.)
Germany	287,000	,,
United States	81,400	,,
Holland and Belgium	55,000	,,
France	52,900	,,
Other European countries	88,000	,,
	895,520	,,

Of the German production, only 30,000 tons were produced from gas works, the remainder being derived chiefly from coke ovens.

Coal always contains nitrogen in greater proportion than is present in fresh vegetable matter, this being probably due to the remains of animals inhabiting the coal-forming forests and swamps. The total percentage of nitrogen found in the coal usually varies between the limits of 0·9 and 2·0 p.c.; thus Tidy (Lunge's Coal Tar and Ammonia, 4th ed. p. 872) found in Welsh coal 0·91 p.c., in Lancashire coal 1·25 p.c., and in Newcastle coal 1·32 p.c., whilst Foster (Inst. Civ. Eng. 77, iii. 23) found in Welsh anthracite 0·91 p.c., in English coals 1·66–1·75 p.c., and in Scotch cannel 1·28 p.c. Schilling (J. Gasbel, 1887, 661), using the Kjeldahl method of estimation, obtained from Westphalian coal 1·50 p.c., from Saar coal 1·06 p.c., from Silesian coal 1·35 p.c., from Bohemian coal 1·36 p.c., from Saxon coal 1·20 p.c., from Boldon (Durham) coal 1·45 p.c., from Pilsener cannel 1·49 p.c., and from Bohemian liguite 0·52 p.c. McLeod (J. Soc. Chem. Ind. 1907, 137) analysed 80 samples of Scotch coals and cannels, and found percentages of nitrogen varying from 0·91 to 1·87, and averaging 1·43.

The world's production of coal in 1909 amounted to about 950,000,000 tons, containing on the average probably some 1·3 p.c. of nitrogen, which, if the whole were recovered as ammonia, would represent an output of about 48,000,000 tons of ammonium sulphate per annum. In fact, however, the production, as shown by the above figures, only amounts to about $\frac{1}{140}$ of this quantity. Fully 90 p.c. of the coal is consumed in such a manner that the recovery of the nitrogen is impracticable, and where the processes in use are such that ammonia is recovered, only a relatively small proportion of the nitrogen is actually obtained in the form of ammonia, for reasons discussed later in considering the different manufactures in which it is produced.

(*a*) *Production of ammonia in the manufacture of coal gas, and of coke in by-product coke ovens.*—The carbonisation of coal in retorts for the manufacture of illuminating gas for general distribution at present yields the largest contribution of ammonia, but the output from this source is being rapidly approached by that obtained in the analogous process of carbonising the coal in ovens for the manufacture of hard metallurgical coke. Formerly the great bulk of such coke was manufactured in beehive ovens, in which case no by-products were recovered, but these are now being rapidly replaced by by-product recovery ovens, the quantity of ammonium sulphate obtained from this source in the United Kingdom having increased from about 10,000 tons in 1899 to 83,000 tons in 1909.

In both industries, however, only a portion of the nitrogen of the coal is recovered in the form of ammonia, the remainder being distributed in the coke, as nitrogenous compounds in the tar, as cyanide in the gas and ammoniacal liquor, and as free nitrogen in the gas. The relative proportion of the nitrogen obtained in the different forms varies considerably, being dependent both on the nature of the coal and on the conditions of carbonisation; the rate at which the latter proceeds, and especially the temperature employed have a marked influence. At low temperatures, such, for example, as are employed in the manufacture of 'coalite' (about 450°), a very large proportion of the nitrogen remains in the coke, but with higher temperatures, although more nitrogen is given off from the coke primarily in the form of ammonia, this is partly converted into hydrocyanic acid by the action of incandescent carbon

and partly dissociated into its elements, the latter being especially the case when the volatile products as well as the residual coke are strongly heated. The maximum yield of ammonia, when carbonising in horizontal retorts appears to take place at a temperature of about 900°–950°, but with vertical retorts heated to much higher temperatures, a greater yield of ammonia is claimed, owing to the fact that the volatile products are not raised to so high a temperature before escaping from the retort.

The following tables, which give figures obtained over a long period of working in gas-works and coke ovens respectively, probably represent a fair average of the distribution of the nitrogen in the two industries under modern conditions, although doubtless in different works considerable variations from these figures occur. The gas-works figures are given by McLeod (J. Soc. Chem. Ind. 1907, 137) as the result of working at the Provan Gas Works, Glasgow, and the coke-oven figures by Short (J. Soc. Chem. Ind. 1907, 581) for the working of Otto-Hilgenstock Coke Ovens, using Newcastle coal.

	Gas works	Coke ovens	
Nitrogen in coke	58·3	43·31	p.c. of total
„ in tar	3·9	2·98	„
„ as ammonia	17·1	15·16	„
„ as cyanide	1·2	1·43	„
„ as free nitrogen in the gas	19·5	37·12	„

McLeod does not appear, however, to include in his cyanide figures the hydrocyanic acid removed from the gas during condensation, allowance for which would probably raise the cyanide figure to about 1·5 p.c.

In both gas and coke-oven works the ammonia is recovered by cooling the gas, when tar and aqueous vapour condense, the condensed water removing a large portion of the ammonia and other gaseous impurities from the gas, and the remainder being recovered by washing the cooled gas with water. Recently, also, in coke-oven works, processes have been adopted in which the ammonia is directly recovered from the hot gas by washing with sulphuric acid after removal of the tar. Methods for manufacturing ammonium sulphate direct from the crude gas, in which the sulphuretted hydrogen present is simultaneously oxidised to form the necessary sulphuric acid, have been described by Feld (Eng. Pat. 3061, 1909) and Burkheiser (Eng. Pat. 20920, 1908; 21763, 1908; 17359, 1910), but the processes are still (1910) in the experimental stage.

The various apparatus employed and methods of working are described in the articles on GAS (COAL) and COKE. The yield of ammonia in both gas works and coke ovens, calculated as sulphate, amounts usually to 20–25 lbs. per ton.

Many attempts have been made to increase the proportion of nitrogen converted into ammonia, but none applicable to these two industries has had any success. Cooper's lime process (Eng. Pat. 5713, 1882), in which lime is added to the coal before carbonisation, was tried in many works, and abandoned, as, although a greater yield of ammonia was obtained, the gain in this respect was more than counterbalanced by the loss due to depreciation in the quality of the resulting coke.

(*b*) *Production of ammonia in the manufacture of producer gas from coal.*—In the manufacture of producer gas from carbonaceous fuel (*see* GAS, PRODUCER) by the introduction of limited amounts of air and steam into the incandescent fuel, the whole of the carbon of the latter is gasified together with the nitrogen it contains. Where the quantity of steam added is limited, so as to ensure that the gas produced shall only contain small percentages of carbon dioxide, the temperature of the producer is such that almost the whole of the ammonia formed from the nitrogen is dissociated into its elements as fast as it is produced. If, on the other hand, a large excess of steam is employed, the temperature of the producer is so much lowered that the greater part of the ammonia escapes decomposition, and may then be recovered from the gas evolved. The latter contains much larger percentages of hydrogen and carbon dioxide than that obtained by the use of smaller quantities of steam, but is still capable of economic employment, especially in gas engines. The process is therefore now largely adopted for producers using bituminous fuel, especially in the Mond Gas plant, in which up to about 75 p.c. of the nitrogen in the coal is recovered as ammonia. This is usually obtained direct as sulphate by washing the crude gas with dilute sulphuric acid, and subsequent evaporation and crystallisation of the solution obtained; the sulphate thus produced has, however, generally a yellow or brownish colour, due to the presence of small amounts of tarry matter.

The employment of steam, except in very limited quantity, is impracticable in the carbonisation of coal in gas works and coke ovens, as the chief products required in those industries are gas of relatively high illuminating power and calorific power, or good coke, or both; and the addition of steam in such quantity as materially increases the yield of ammonia, effects so large a depreciation in the quality of gas and coke produced that the loss in these respects far outweighs any increased revenue obtained from the additional quantity of ammonia formed.

(*c*) *Production of ammonia from shale.*—In the distillation of Scotch bituminous shales for the production of shale oil (*see* PARAFFIN), ammonia is also evolved, and is recovered in a similar manner to that employed in gas works. In this case also the introduction of steam (and also of limited quantities of air) during the distillation has the effect of largely increasing the percentage of nitrogen recovered as ammonia. The objections to the method which hold in the case of the gas industry do not apply in the shale-oil manufacture, as the chief product, the shale oil, is not materially affected by the use of steam, and the coke formed is in any case of little value. The gas produced, even when steam is used, is sufficiently good for the purpose for which it is used, namely, for heating the retorts. The addition of steam for increasing the yield of ammonia was, in fact, first worked out to practical success in this industry, chiefly by Young and Beilby (Eng. Pat. 1587, 1881; 2164, 1881; 4284, 1881; 1377, 1882; 5084, 1882; see also Beilby, J. Soc. Chem. Ind. 1884, 216), its application in the case of carbonisation of coal in producers for the same purpose being of rather later date.

(*d*) *Ammonia from blast furnaces.*—Where coal is used as fuel in blast furnaces for cast-iron production, the waste gases contain considerable quantities of ammonia and tarry matters, which are now largely recovered from the gas, the latter, after purification, being employed in gas engines. In most English districts, the coal available is not sufficiently hard for use in the furnaces, and hard coke is used, the employment of coal being confined chiefly to the West of Scotland and to North Staffordshire, where coal of sufficient hardness can be obtained. The recovery of the tar and ammonia is effected by cooling and washing in a similar manner to that employed in gas works, the apparatus being suitably modified to allow for the fact that the tar and ammonia are much more diluted with other gases, and that large quantities of dust are mechanically carried along with the gas from the blast furnace. Processes for the washing of the gas with dilute sulphuric acid do not appear so far to have been permanently successful, and the same is true of the process of Addie (Eng. Pat. 4758, 1882; 3246, 1883), in which the gas was mixed with sulphur dioxide and passed through a scrubber fed with water, the resulting solution of ammonium sulphite being oxidised to sulphate by injection of air.

The yield of ammonium sulphate obtained from blast furnaces is very similar to that obtained in gas works and from coke ovens, namely from 20 to 25 lbs. per ton of coal.

(*e*) *Ammonia from peat.*—Vast deposits of peat exist in many places, especially in Ireland and Prussia, and as this contains a good deal of nitrogen, amounting in some cases to 4 p.c. of the dry peat, many attempts have been made to recover this nitrogen as ammonia. The great difficulty in the way has been the very large quantity of water contained in the peat, which is costly to remove, and hitherto very little ammonia has been put on to the market from this source. Of the earlier attempts that of Grouven (D. R. PP. 2709, 13718, 18051) is of interest, inasmuch as this represents one of the first attempts to increase the yield of ammonia by injection of steam during distillation, but although prolonged experiments were made with the process, it was ultimately abandoned. Lencauchez suggested the use of peat in gas producers with subsequent ammonia recovery, and patents relating to the matter were taken out by Ruderer, Loe, and Gumbart (D. R. P. 53844), Kuntze (Eng. Pat. 9052, 1891), and Pieper (Eng. Pat. 28190, 1896).

More recently Woltereck (Eng. Pat. 16504, 1904; 28963, 1906; 28964, 1906) has patented a process for recovering ammonia and other products from peat, and works for carrying out the method have been erected near Carnlough Harbour, in the North of Ireland. In his process, the wet peat is placed in a generator, and burned in a current of air and steam, regulated so as to keep the temperature of the generator very low and at the same time to effect almost complete combustion of the peat, no attempt being made to obtain a combustible gas. The products, in addition to the waste gases, are chiefly small quantities of tarry matter of the paraffin series, acetic acid and ammonia, the first being removed by treating the hot gases with high boiling oils, the gas then passing through hot milk of lime to absorb the acetic acid, and finally through sulphuric acid to recover the ammonia as sulphate. (It is claimed that not only is a quantitative yield of ammonia obtained from the nitrogen of the peat, but that some ammonia is also formed synthetically from the nitrogen of the air used.) Details of the results on the manufacturing scale have not yet been published.

Frank and Caro, in conjunction with the Mond Gas Co. (Zeitsch. angew. Chem. 1906, 1569), find that peat containing 50 p.c. of water may be employed in place of coal in the Mond Gas plants, with production of gas suitable for gas engines, and a yield of about 90 lbs. of ammonium sulphate per ton of dry peat.

(*f*) *Ammonia from bones, horn, leather, hair, skins, and other animal refuse.*—In the distillation of bones for the manufacture of bone charcoal (animal charcoal, or 'char'), used especially in sugar refining, large quantities of ammonia are formed, together with tar rich in pyridines, known as 'Dippel's oil.' The carbonisation is frequently carried out, especially in France and Germany, by heating the bones in open pots placed in a furnace, in which case the tar and ammonia are so largely diluted with hot furnace gases that their recovery is rendered very difficult. In this country generally, and to an increasing extent elsewhere, the carbonisation is effected in closed retorts, and the tar and ammonia recovered in accordance with the usual gas works practice, the yield of ammonia being equivalent to about 50–60 lbs. of sulphate per ton of dry bones.

Other animal refuse, such as wool, hair, skin, waste leather, &c., is sometimes carbonised in a similar way, the residue being employed as manure, and the ammonia recovered from the gases. Sometimes, however, these materials are simply heated in cylinders in a current of steam, which renders them friable and capable of ready disintegration, when they are directly employed as manure. A further proposal is to utilise the nitrogen by heating the dried refuse with concentrated sulphuric acid, whereby the nitrogen is converted quantitatively into ammonium sulphate, as in the well-known Kjeldahl method of estimating nitrogen.

(*g*) *Ammonia as a by-product in the beet-root sugar industry.*—During the evaporation of beet-root juice, small amounts of ammonia are evolved, which Vibrans (D. R. P. 15513) has proposed to collect. Much larger amounts can, however, be obtained by the distillation of the 'vinasse,' *i.e.* the residue left after fermenting the sugar remaining in the molasses, and distilling off the alcohol produced. This contains nitrogenous bases, especially betaïne, and on dry distillation yields ammonia and trimethylamine. Vincent (Chem. News, 39, 107) carried out the distillation with the primary object of obtaining trimethylamine and from the latter methyl chloride, but the ammonia was simultaneously recovered as sulphate. The residue from the distillation is rich in potassium salts, and is employed as a manure or worked up into pure salts. Other patents dealing with the recovery of ammonia by distillation of vinasse are those of Ernst (D. R. P. 13871), Lederer and Gintl (D. R. P. 17874), and Meyer (Eng. Pat. 17347, 1887). Bueb (Eng. Pat. 7175, 1895;

26259, 1898; see also Ost, Zeitsch. angew. Chem. 19, 609) utilises the vinasse for the production of both ammonia and cyanides, the latter being the product especially aimed at. In his process the vinasse is carbonised in retorts in the ordinary manner, and the gases, which contain ammonia and trimethylamine, but little hydrocyanic acid, are then passed through a highly heated brickwork chamber, the ammonia being only slightly affected, whilst the trimethylamine is converted chiefly into hydrocyanic acid. The resulting gases, containing about 7 p.c. of ammonia and 7 p.c. of hydrocyanic acid, are passed through sulphuric acid to recover the ammonia as sulphate, and the gas freed from ammonia employed for the manufacture of cyanide.

II. Properties and Composition of Ammoniacal Liquor. The ammoniacal liquor obtained by the washing and cooling of the gases produced by destructive distillation, is, after separation from tar by settling, a liquid having a colour from pale yellow to dark brown, and smelling strongly of ammonia, sulphuretted hydrogen, and also of phenols. Its specific gravity usually varies from 1·01 to 1·03. In the coal-gas manufacture, the liquor is usually obtained in three stages, viz. (1) the hydraulic main liquor, formed during the cooling of the gas to temperatures of 50°–60°, which is usually weak (0·5–1·0 p.c. of NH_3), owing to the lessened solubility of ammonia at that temperature; (2) the condenser liquor, produced in the subsequent cooling of the gas to atmospheric temperature, which is more concentrated (2–3·5 p.c. of NH_3); and (3) the scrubber and washer liquor, formed by washing the cooled gas to effect complete removal of the ammonia, the strength of which varies considerably, and depends largely on the construction of the washing plant, and the supervision of the working. The first two products together form the 'virgin liquor,' *i.e.* solution produced from the water formed by the condensation of the steam always present in the crude gas; but the liquor from all sources is usually collected together with the tar in a common storage well or wells. Frequently the weak hydraulic main liquor is used, after cooling, in the preliminary washers or scrubbers, thereby effecting a further partial removal of the ammonia, and becoming simultaneously concentrated, but for the complete removal of the ammonia the gas must be washed with fresh water in the final scrubber. In coke-oven works the conditions prevailing in these respects are very similar generally to those in gas works.

The quantitative composition of the ammoniacal liquor varies considerably, not only in that obtained at different stages of the process, but also in the average liquor obtained, being dependent on the nature of the coals carbonised, the conditions of carbonisation, and the construction and working of the condensing and scrubbing plant. The qualitative composition varies but little; the primary products formed in the liquor are ammonium chloride, sulphides, carbonates, and cyanide, produced by the action of the ammonia solution on the acid constituents of the crude gas, viz. hydrochloric acid, sulphuretted hydrogen, carbon dioxide, and hydrocyanic acid. The strongly acid hydrochloric acid is absorbed in the earlier stages of the cooling, chloride being only present to any extent in the hydraulic main and condenser liquor, but the total quantity of ammonia present is insufficient to remove the whole of the remaining acid gases, which are separated later by special purification processes. Other ammonium salts are, however, produced in the liquor by secondary reactions; thus the sulphide is oxidised by the oxygen always present in the crude gas, and later by the oxygen of the air to which it is exposed during storage, yielding polysulphides, thiosulphate, sulphate, and possibly sulphite. The cyanide reacts with the polysulphide, forming thiocyanate, and possibly also with thiosulphate, forming thiocyanite and sulphite, so that polysulphide is rarely if ever found in the liquor. Small quantities of ferrocyanide are also sometimes formed by the action of ammonium cyanide on the ironwork of the apparatus. In addition, the liquor always contains small quantities of pyridine, and considerable amounts of substances derived from the tar, especially phenols.

From the point of view of the subsequent working up of the ammoniacal liquor, it is important to distinguish between the amount of 'volatile' and 'fixed' ammonia present. The former represents the ammonia present as sulphide, carbonate, and cyanide, and in combination with the phenols, the term being given because the ammonia in this form is completely dissociated and volatilised by simply boiling the solution; whereas that present as chloride, sulphate, thiosulphate, and thiocyanate is not evolved to any material extent under these conditions, and is therefore termed 'fixed' ammonia. For its recovery it is necessary to add to the liquor a sufficient amount of a stronger alkali to combine with the whole of the above-named acids present. The 'fixed' ammonia in the average liquor usually amounts to from 20 to 25 p.c. of the whole, but the proportion is much higher in the hydraulic main and condenser liquor.

The table on p. 145 gives the results of a number of analyses of ammoniacal liquor from gas-works, coke-ovens, shale-works, and iron-works, made by Linder, on behalf of the Chief Alkali Inspector, and published in the annual reports of the latter. In addition an analysis is also given of the liquor obtained in low-temperature carbonisation as practised in the coalite manufacture, and two analyses of German gas-works liquor, by Mayer and Hempel (J. Gasbel, 1908, 428). (For methods of analysis, *see* Linder (Alkali Inspector's Report, 1909, 15), and Mayer and Hempel (*l.c.*).) In these analyses the whole of the carbon dioxide and sulphuretted hydrogen present is calculated as the normal carbonate and sulphide respectively, and in Linder's analyses the difference between the total sulphur and that present as sulphide, sulphate, and thiocyanate is calculated as ammonium thiosulphate.

The existence of free ammonia (or its hydroxide) is a point on which considerable difference of opinion exists. The above analytical results appear to show that in the case of average stored liquor, the quantity of acids present, including phenol, is usually sufficient to combine with the whole of the ammonia

but at the same time it is very probable that some of the salts, especially the sulphides and carbonates, undergo hydrolytic dissociation into acid and free ammonia or its hydroxide in the solution. With the hydraulic main liquor, formed at temperatures mostly above 60°, the acids found are insufficient to combine with the whole of the ammonia, some of which must therefore be present in the free state. The existence of free ammonium cyanide in the liquor has also frequently been denied, but more perfect methods of analysis have shown that this is undoubtedly often present in small quantity even in stored gas-works liquor, and that in coke-oven liquor, which is usually only stored for a short time before working up, the amount may be considerable. The presence of cyanide is objectionable, as it increases the amount of hydrocyanic acid in the waste gases from the manufacture of ammonium sulphate (*see* below).

III. Valuation of Ammoniacal Liquor. In this country, for technical purposes, the strength of the ammoniacal liquor is mostly expressed in terms of 'ounce-strength,' this figure representing the number of ounces avoirdupois of pure sulphuric acid required to neutralise the ammonia contained in 1 gallon of the liquor, and for statistical purposes or sale, the volumes of liquor are usually converted into the equivalent volume of liquor of 10-oz. strength. In order to convert these figures into the more generally familiar ones of grams per 100 c.c., the 'oz.-strength' figures must be multiplied by 0·217, and conversely, to convert figures representing grams per 100 c.c. into oz.-strength, the former must be multiplied by 4·61.

For approximate purposes the ammonia content of the liquor is frequently estimated from the density, it being found that each 1° Twaddell corresponds roughly to 2-oz. strength. This approximation is sufficient for such purposes as the control of the daily working of the washers and scrubbers on the works, but quite unsuitable for purposes where fair accuracy is desired, as a liquor showing 5°Tw., for example, may vary in actual content from 8- to 12-oz. strength, as against the supposed 10-oz. For any but the roughest purposes, ammonia is estimated by the usual method of distilling a known volume, after addition of alkali to decompose the fixed salts, collecting the distillate in excess of standard acid, and titrating the unused acid with standard alkali. The liquid must not be distilled to dryness, as otherwise the thiocyanates may be decomposed with formation of ammonia, giving too high results.

IV. Working up of Ammoniacal Liquor. In the earlier days of the utilisation of gas liquor, this was simply neutralised with sulphuric or hydrochloric acid, and the resulting solution evaporated, but the products obtained were very impure, containing tarry matter and thiocyanate, and the escaping gases, especially the sulphuretted hydrogen, created great nuisance. At present the ammonia is almost

COMPOSITION OF AMMONIACAL LIQUOR.

—	Gas works					Coke ovens	Blast furnaces		Shale works	Coalite works	—
	Average of five samples of stored liquor.—English works	Stored well liquor.—German works	Hydraulic main liquor.—English works	Hydraulic main liquor.—German works	Condenser liquor.—English works	Average of nine samples of liquor	Liquor from coolers only	Liquor from washers only	Average liquor from storage well.	Average liquor circulated through washers to get up strength	
											grams per 100 c.c.
Volatile ammonia	1·929	1·406	0·721	0·291	3·247	0·841	0·191	0·362	0·873	1·547	"
Fixed "	0·613	0·309	0·306	0·288	0·221	0·102	0·008	0·009	0·032	0·170	"
Total "	2·542	1·715	1·027	0·579	3·468	0·943	0·199	0·371	0·905	0·717	"
Ammonium sulphide $(NH_4)_2S$	0·862	0·276	0·276	0·073	0·768	0·466	nil	?	0·098	0·230	"
" carbonate $(NH_4)_2CO_3$	5·000	3·526	1·320	0·475	8·810	1·960	1·104	?	2·870	6·360	"
" chloride NH_4Cl	1·120	0·738	0·838	0·722	0·459	0·217	0·006	?	0·015	0·106	"
" sulphate $(NH_4)_2SO_4$	0·202	0·023	?	0·023	?	0·032	0·009	?	0·016	0·054	"
" thiosulphate $(NH_4)_2S_2O_3$	0·173	0·123	?	0·143	?	0·041	0·002	?	0·090	0·407	"
" thiocyanate NH_4CNS	0·528	0·182	0·047	0·100	0·070	0·043	0·003	0·003	nil	0·335	"
" cyanide NH_4CN	0·036	0·003	0·034	0·003	0·070	0·070	nil	0·003	nil	nil	"
" ferrocyanide $(NH_4)_4Fe(CN)_6$	0·038	0·088	0·019	0·019	0·030	nil	nil	nil	nil	nil	"
Authority	Linder	Mayer and Hempel	Linder	Mayer and Hempel	Linder	Linder	Linder	Linder	Linder	Linder	

The quantity of phenols present in gas-works liquor usually varies from 0·1 to 0·35 grams per 100 c.c. (Skirrow, J. Soc. Chem. Ind. 1908, 58).

invariably recovered from the liquor in the first instance by distillation. Formerly, also, in many cases, only the volatile ammonia was recovered, as this could be obtained without addition of alkali, the fixed ammonia being run off with the waste liquor; but this procedure is now becoming exceptional, the fixed ammonia, except in the case of some small plants, being also mostly recovered by addition of the necessary alkali. On account of its cheapness, lime is almost always employed for this purpose, but in some small plants, caustic soda is used, for although the cost of the latter is much greater, this is held by some makers to be compensated for in such plants by the fact that the stills run much longer without cleaning.

The plant employed in the distillation has been of various types; at first an intermittent process of distilling the liquor in externally fired boilers was adopted, the distillation being continued until the whole of the volatile ammonia was expelled with the steam. Addition of lime to drive off the fixed ammonia was rarely practised with such plants, owing to the formation of thick deposits of lime salts on the heated boiler plates. These plants have now been almost entirely superseded by continuous column stills, constructed on the general principle of the Coffey still, the intermittent system being now employed only in very small works or in special cases, such as the distillation of liquors containing very large quantities of fixed ammonia, in which case the addition of the necessary amount of lime renders the liquid so thick that these must be stirred by mechanical agitators to effect complete recovery of the ammonia. The annual report of the Chief Alkali Inspector for 1909 shows that in the various districts into which the United Kingdom is divided for administration purposes under the Alkali Act, the proportion of liquor distilled by intermittent stills varies from about 7 p.c. to *nil*,

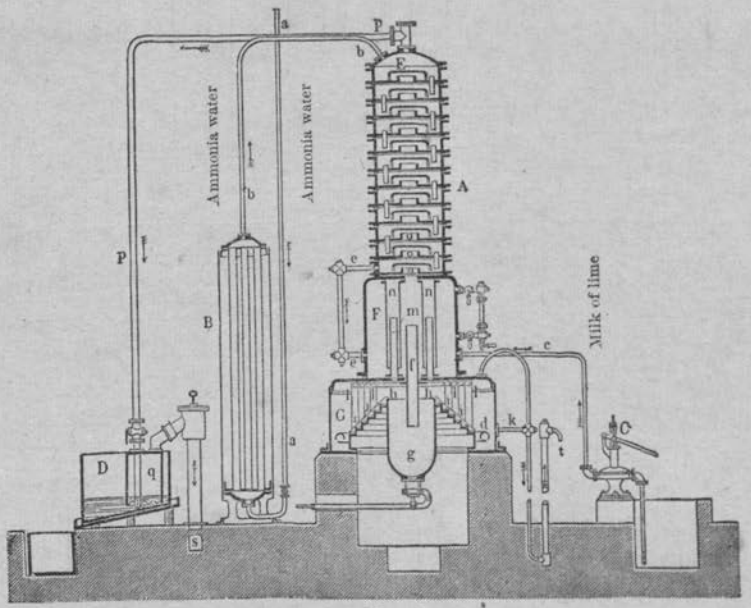


FIG. 1.

and probably averages over the whole country from 1 to 2 p.c.

For the purpose of heating the stills, three methods have been employed: (1) external firing; (2) by means of internal coils through which steam is passed; and (3) by blowing live steam through the stills. The first plan gives a high fuel consumption, as well as trouble from lime deposits on the heated portions of the still; and of the other two methods the use of live steam is the most economical in fuel consumption, and is therefore now almost invariably adopted.

The ammonia evolved on distillation is converted at once either into ammonium sulphate, concentrated gas liquor, pure aqueous ammonia, or liquefied ammonia. The remaining salts of commercial importance, namely, ammonium chloride, carbonate, and nitrate, are now rarely manufactured directly from the ammonia as evolved from the stills, but are obtained either from ammonium sulphate or aqueous ammonia previously prepared from the gas liquor. Much the largest proportion of the liquor is converted into sulphate, the demand for this salt being greatest, owing to its employment as a nitrogenous manure. The method of manufacture of this salt will therefore be described first, followed by that of the other commercially important ammonia derivatives.

Ammonium sulphate.—A description of the different forms of intermittent still formerly adopted for obtaining the ammonia in the liquor, but now seldom used, may be found in Lunge's Coal Tar and Ammonia 4th ed. Of the continuous stills, those of Grüneberg and Blum (D. R. P. 33320) and of Feldmann (Eng. Pat. 3643, 1882) will be described, more recent forms differing from these only in detail and not in general principles. In the manufacture of sulphate, the volatile ammonia is first driven off, lime being then added to the liquor to liberate the fixed ammonia,

the combined gases evolved being passed through sulphuric acid.

The apparatus of Grüneberg and Blum is shown in Fig. 1, as arranged for the manufacture of sulphate. A is the still, B the gas-liquor heater or economiser, C the lime pump, and D the saturator charged with acid for absorption of the ammonia. The gas liquor enters the economiser B by means of pipe *a*, and is heated by the hot waste gases from the saturator, and passes thence by the pipe *b* to the top of the column E of the still. This column is divided into a number of compartments by horizontal division plates, the liquor flowing downwards from compartment to compartment by the overflow pipes, the admitted steam travelling upwards in the reverse direction through the central pipes *o*, covered by hoods having serrated edges, which compel the steam to bubble through the liquor in each compartment, thus driving off the 'volatile' ammonia and also the volatile acids present, viz. carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid.

The lime vessel F, into which milk of lime is pumped by means of pump C and pipe *c*, serves to expel the fixed ammonia, and the boiler G, with its stepped cone, serves to boil the liquor in thin sheets, by means of the steam coil *d*, and thus to set free the last portions of ammonia. In B the first heating of the liquor takes place by means of the hot vapours from the saturator D, which ascend through the bell *q*, the pipe *s*, and the inner pipes of B, while the liquor, arriving at *a*, rises up in B. It then enters through *b* into the dephlegmating column E, and finds its way downward from chamber to chamber, till it gets into the lime vessel F. From here it overflows by pipe *f* into the sludge-catcher *g*, overflows here again all round at *hh*, and runs over the cone *i* downwards from step to step; from the pipe *k* it is discharged continuously and quite spent to the overflow *t*. The steam travels in the opposite way—namely, along the steps of cone *i*, upwards in pipe *m*, and through *n* into the lime vessel F. From here the mixed steam and ammonia vapours ascend into the column E, and traverse this from chamber to chamber, and ultimately leave it by the pipe *p*. This pipe enters the saturator D, charged with sulphuric acid. The sulphuretted hydrogen, carbon dioxide, &c., collecting in the bell *q*, are led through the flue *s* into the economiser B, where they give up their heat to the gas liquor, and lose their steam in the shape of condensed water. Ultimately they are conveyed away by a pipe not shown in the diagram for treatment to prevent nuisance, the methods adopted for the purpose being described below.

In the apparatus of Feldmann (D. R. P. 21708), Fig. 2, the gas liquor, after having passed through the ordinary rectifying column A, flows into a vessel B, into which milk of lime is pumped by G in regular intervals, whilst the whole is kept agitated by steam injected into the mixture. The liquor, after having deposited most of the lime, flows into a second column C, where the ammonia set free by the lime is distilled off: the spent liquor runs away continuously through *g*, and the gases and vapours pass over by pipe *h* into the first column BA, which serves both for retaining the water and for driving off the volatile ammonium salts contained in the crude gas liquor. The economiser J, and the saturator B, with the gas-bell F, require no special explanation.

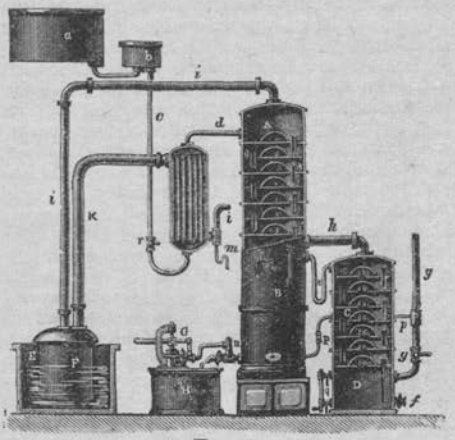


FIG. 2.

In more recent types of still, only a single column is usually employed, the lime being introduced into one of the compartments of the lower portion of the still, which may be made of larger size for this purpose, the hood being also more deeply sealed to effect more vigorous agitation. The mixture of liquor and lime then passes through the lower compartments of the still, constructed in a similar manner to those above. A still of this type, manufactured by the Berlin Anhaltische Maschinen Actien-Gesellschaft is shown in Fig. 3.

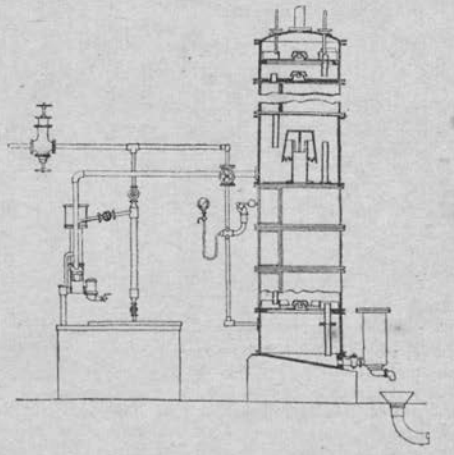


FIG. 3.

Other modifications relate chiefly to improvements in mechanical details, and in making the parts more accessible for cleaning, especially in the portions of the still where lime is present. Thus Wilton (Eng. Pat. 24832, 1901) replaces the central pipe for the steam and circular hood, by a narrow opening extending over nearly the full diameter of the still, and covers this with an inverted trough having serrated edges, which can readily be removed for cleaning from

a small manhole at the side. Scott (Eng. Pat. 3987, 1900; 11082, 1901) has patented a process in which the whole of the plant is kept under vacuum, whereby considerable economy of fuel is claimed. The plant and method of working are described by Ballantyne (J. Gas Light. 82, 869).

Absorption of the ammonia in sulphuric acid.—The gases from the still, consisting chiefly of ammonia steam, carbon dioxide, sulphuretted hydrogen, and small quantities of hydrocyanic acid, are conveyed to the saturator (D in Fig. 1, E in Fig. 2) charged with sulphuric acid. This is constructed either of solid lead throughout, or of wood or iron lined with lead, the gases being conducted in by means of a perforated leaden pipe which distributes them over a large area in the saturator and keeps the liquid thoroughly agitated. In some cases, dilute sulphuric acid is used, this being removed and replaced by fresh acid when nearly neutralised. The solution, after settling, is concentrated and crystallised, the mother liquor being returned to the saturator. The dilute solution of ammonium sulphate obtained by direct washing of the crude gas with acid, as in the Mond Gas process, is evaporated and crystallised in a similar way. In most cases, however, when distilling gas liquor, a much stronger acid (of about 140°Tw.) is used which soon becomes saturated, after which the ammonium sulphate crystallises out as formed, and is removed by various means, fresh acid being run in to replace that removed as sulphate. Two types of saturator are employed, (*a*) partly open, (*b*) closed. A common construction of the former type is shown in Fig. 4, the gases

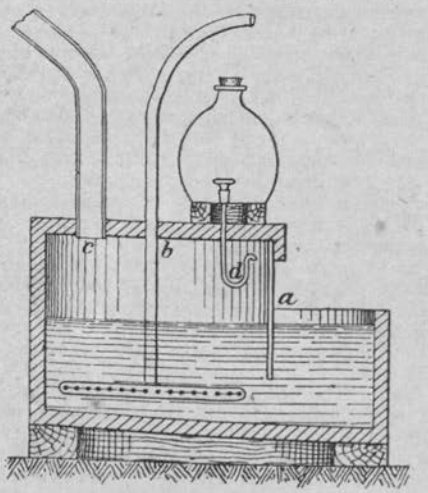


FIG. 4.

entering by the pipe *b* perforated as shown, and bubbling through the acid, the waste gases being led off by the pipe *c*; the sulphate accumulates on the floor of the saturator. The front of the saturator is open, and separated from the closed portion by the sealing curtain *a*, which does not reach to the bottom, and enables the attendant to remove the sulphate periodically by fishing with a perforated ladle, the crystals being placed on a lead-lined drainer fixed so that the mother liquid flows back to the saturator. When sufficiently dry, the product is placed into stock, or it may be at once dried by a centrifugal machine.

In place of 'fishing,' the sulphate may be periodically or continuously removed from the saturator by means of a steam-ejector, which forces it together with much liquor on to the drainer, thence into a centrifugal machine, the mother liquor in either case returning to the saturator.

With a closed saturator other means of removing the sulphate are adopted, a representative of this type being the Colson saturator,

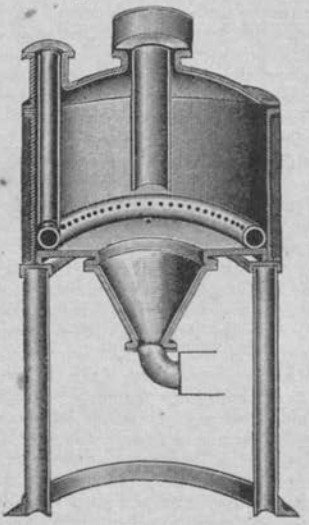


FIG. 5.

the bottom of which consists of an inverted cone, to the apex of which is fixed a right-angled bend, closed by a simple valve, consisting of a copper disc pressed against the flange of the outlet pipe by a screw clamp. During working this is opened to a sufficient extent to allow the sulphate to fall out almost as soon as it is formed.

The ammonium sulphate thus obtained usually contains from 24 to 25 p.c. of ammonia, equivalent to about 93–99 p.c. of pure ammonium sulphate. It usually contains from 0·1 to 0·5 p.c. of free sulphuric acid, the remainder consisting of moisture and small quantities of insoluble matter. The salt produced with modern plant has mostly a white or greyish-white colour, discolouration by tarry matter being now of rare occurrence with continuous stills, if the liquor is properly separated from tar by settling previous to distillation. When pyrites sulphuric acid is employed, the resulting sulphate may be coloured yellow or brown, by arsenic sulphide, which depreciates its value, and makers therefore prefer to use acid obtained from brimstone or spent oxide. In many cases, however, pyrites acid is used, and the arsenic sulphide which rises as a scum to the surface of the liquid in the saturator removed as it forms, or preferably the acid is previously treated with a portion of the waste gases from the saturator, the sulphuretted hydrogen in which precipitates the arsenic as sulphide, the latter being removed before the acid enters the saturator.

In some cases the sulphate assumes a blue colour on standing in the air, owing to the formation of traces of Prussian blue. From the researches of Forbes Carpenter and Linder (Chief Alkali Inspector's Report, 1905, 51), it appears that this is mostly due to local alkalinity occurring in some portion of the liquid in the saturator, in which case hydrocyanic acid is absorbed at that point, and, with the traces of iron always present, forms ammonium ferrocyanide; the latter, on exposure to the air, oxidises, forming Prussian blue. Priming of the still, resulting in the introduction of ferrocyanides and thiocyanates into the saturator, has a similar effect, but the production of the blue salt often occurs in absence of priming. Its formation is best avoided by maintaining the liquid hot and of sufficient acidity, and arranging that the passage of the gas shall effect a thorough mixing of the liquid in the saturator, so as to prevent the occurrence of local alkalinity.

Waste products in the manufacture of Ammonium Sulphate.—Three waste products are formed in the process: (*a*) the effluent liquor; (*b*) the aqueous condensate from the cooling of the waste gases; (*c*) the waste gases. The effluent liquor is run into settling tanks, where it deposits suspended lime salts, and becomes cooled. The clarified liquor is sometimes run into the sewers, but as it contains large quantities of lime salts (especially thiocyanate and phenols), this is frequently not permitted, and its disposal is often a matter of great difficulty. In gas works it is sometimes got rid of by employing it to quench the hot coke from the retorts, and in some cases it is even evaporated to dryness. Fowler (Alkali Inspector's Report, 1907, 51) allows the liquor, after considerable dilution, to pass through coke filters inoculated with sewage bacteria, which, if gradually accustomed to the liquor, oxidise the thiocyanates and phenols, yielding a fairly pure effluent, and this may be employed for dilution of the fresh liquor going on to the filter. Radcliffe (Eng. Pat. 10075, 1905) removes the thiocyanates by precipitating as cuprous thiocyanate with copper sulphate in presence of sulphurous acid, the latter being obtained by burning a portion of the waste gases. Grossmann (Eng. Pat. 20387, 1905; 7932, 1907; J. Soc. Chem. Ind. 1906, 411) has also described a process for avoiding the production of waste liquor and recovery of the ferrocyanide and thiocyanates present in it.

The avoidance of the production of waste liquor altogether is an especial object in the process of the Otto-Hilgenstock Coke Oven Co. (Eng. Pat. 12809, 1908) now being adopted in some coke-oven works. In this the gas from the ovens is treated for the removal of tar at temperatures above that at which water condenses, and then passed directly through sulphuric acid; the aqueous condensate obtained in the subsequent cooling of the gas is free from ammonia, and only contains small amounts of impurity, and it is claimed that no difficulty is experienced in disposing of it. Wilton (Eng. Pat. 16355, 1909) has patented a somewhat similar process with the same object.

The aqueous condensate obtained by cooling the waste gases is a very noxious-smelling liquid, and is hence termed 'devil-liquor.' It contains sulphuretted hydrogen, pyridines, and similar substances, and hydrocyanic acid, and is also difficult to dispose of. The hot condensate from the liquor-heater or economiser is less objectionable than that obtained in the further cooling of the waste gases, which contains much more sulphuretted hydrogen; but if the latter is returned to the pipe conveying the hot condensate and the waste gases from the economiser, most of the sulphuretted hydrogen is driven off again into the waste gases, and the combined liquor, after cooling, may be mixed with the effluent from the stills without increasing the difficulty of dealing with the latter (Broadberry, J. Gas Light. 69, 345).

The waste gases, after cooling, consist chiefly of carbon dioxide, sulphuretted hydrogen, and smaller quantities of hydrocyanic acid, as well as strongly smelling empyreumatic vapours derived from the tar. With coke-oven liquors, which often contain considerable quantities of cyanide, the amount of hydrocyanic acid may be considerable, necessitating additional care in dealing with it owing to the poisonous nature of the gas. In many cases the gases are burned under the boiler or other furnaces, and discharged with the products of combustion from the chimney; or the gases may be burned separately and the resulting sulphur dioxide absorbed by passing the products through a limestone tower down which water is passing, yielding a solution of calcium bisulphite, or through scrap-iron towers, when a solution of ferrous sulphate is formed (Wilton, Eng. Pat. 15468, 1901). With small and medium-sized plants, the sulphuretted hydrogen and hydrocyanic acid are mostly removed by oxide of iron, in a similar manner to that employed for purifying coal gas. In place of purifying boxes, conical heaps of oxide of iron on a concrete floor are now much used, the gas being introduced from the bottom at the centre of the heap; the spent oxide obtained is saleable for its sulphur content. The sulphuretted hydrogen may also be precipitated with metallic salts, and where sulphuric acid is also made, the gases are burned and passed into the chambers, thus recovering the sulphur as sulphuric acid. A considerable proportion of the waste gas is converted into sulphur by the Claus process (Eng. Pat. 3606, 1882; 5070, 1883; 5958, 1883), also used on the large scale in the Chance sulphur-recovery process. By this method, sufficient air is mixed with the gas to react with the sulphuretted hydrogen in accordance with the equation $2H_2S+O_2=2H_2O+2S$, and the mixture passed through a kiln containing heated ferric oxide, the sulphur formed being deposited in cooling chambers, and the residual gases passed through a small limestone tower and oxide-of-iron purifier to remove any sulphur dioxide or sulphuretted hydrogen remaining. The sulphur obtained is not very pure, owing to tarry matters, &c., present in the gases treated.

Manufacture of Caustic Ammonia (Liquor Ammoniae) and of Liquefied Ammonia.—The pure aqueous solution of ammonia was formerly manufactured by distilling ammonium sulphate with lime in intermittent stills provided with mechanical arrangements for stirring the somewhat thick cream, but it is now usually made by the direct distillation of gas liquor, with suitable purification of the gas evolved from the stills, which is then dissolved in water. In addition

to the pure aqueous solution, a crude solution containing sulphide, and sometimes carbonate, is also largely manufactured, this being cheaper and equally applicable to many purposes, especially in the manufacture of soda by the ammonia-soda process, and for the preparation of other ammonium salts. This crude product is termed 'concentrated gas liquor,' two kinds being manufactured, the one containing from 16 to 18 p.c. of ammonia, with both sulphide and carbonate present, and the other from 18 to 26 p.c. of ammonia, with some sulphide but little or no carbonate.

In the manufacture of the first-named liquor, the gases from the stills, worked as in the manufacture of the sulphate, pass through a reflux condenser, to remove some of the steam present, and then through a direct condenser, the gases from which are washed with water. Working in this manner, it is not practicable to obtain a greater strength of ammonia than 16–18 p.c., as with higher concentrations stoppages occur in the condenser from crystallisation of ammonium carbonate. For the preparation of the more concentrated gas liquor, the vapours from the still, after passing the reflux condenser, are led through a washer containing milk of lime, which removes practically the whole of the carbon dioxide and some of the sulphuretted hydrogen, a liquor being then obtained by condensation usually containing 22–26 p.c. of ammonia, and a little sulphide, but usually free from carbonate.

Pure Caustic Ammonia.—In the manufacture of pure aqueous ammonia from gas liquor, a sufficient quantity of lime must be employed to remove the whole of the acid constituents of the liquor, including the carbon dioxide and sulphuretted hydrogen. For the complete removal of the latter the use of a decided excess of lime is necessary, and owing to the hydrolysis of calcium sulphide even excess of lime does not remove the last traces of sulphuretted hydrogen, which is eliminated by other reagents. The addition of the large amount of lime required in the stills themselves during the distillation of the liquor, gives rise to much trouble from blockage in the latter, and it is therefore mostly found preferable to effect the removal of those two gases by passing the still vapours through lime washers. Much economy in the use of lime results if the liquor, previous to distillation, is subjected to a preliminary heating to 70°–80° (Hills' process), at which temperature a large proportion of the carbon dioxide and sulphuretted hydrogen are evolved, accompanied by only small amounts of ammonia, the latter being recovered by washing the evolved gases with water or weak ammoniacal liquor, or, where the manufacture of sulphate is carried on simultaneously, the gases evolved may be passed direct to the sulphuric-acid saturator, along with the gases from the stills used in that process.

The preheated liquor is distilled as in the case of the sulphate process, and the gases evolved, after traversing a reflux condenser, pass through a set of two or three washers, containing cream of lime, to remove carbon dioxide and sulphuretted hydrogen, the partly used lime being run back into the stills to effect the decomposition of the fixed ammonium salts, and recovery of ammonia from the cream. To ensure the removal of the last traces of sulphuretted hydrogen, ferrous sulphate solution is sometimes added to the last lime washer, the ferrous hydroxide formed by the action of the lime retaining the gas as ferrous sulphide, or, according to Pfeiffer (J. Gasbel. 1900, 89), a small final washer containing caustic soda solution is added. Solutions of sodium permanganate or ammonium persulphate may also be used (Foucar). The gases then pass through a series of scrubbers charged with wood charcoal, which remove the strongly smelling empyreumatic substances derived from the tar, and in some cases additional purification in this respect is effected by passing the gas through a fatty or high-boiling mineral oil. The resulting purified gas is then led into distilled water, and thus converted into solution of any desired strength up to about 36 p.c. The charcoal scrubbers must be renewed as soon as their activity becomes lessened, the spent material being revivified by heating in closed retorts.

Technical caustic ammonia is usually clear and colourless, and contains only small quantities of pyridine and empyreumatic substances. When these are present in larger quantity, owing to defective action of the charcoal filters, the liquid assumes a yellowish colour on keeping. Its strength is ascertained from its specific gravity. A table showing the specific gravity of different concentrations is given on p. 139.

Liquefied Ammonia.—The liquefied gas, stored in steel cylinders, is now largely produced and employed for refrigeration purposes. It is manufactured from the gas obtained and purified as described for the manufacture of the pure aqueous solution, but instead of passing it into water, it is well dried, and then compressed by suitable pumping machinery. The commercial liquid usually contains small amounts of water, pyridine, and lubricating oil, and traces of other substances, but is now sold, in many cases, as of guaranteed 99·9 p.c. purity.

Ammonium Chloride (Muriate of Ammonia or Sal-ammoniac).—This salt has been manufactured in a similar manner to that employed for the sulphate, by passing the gases from the stills into hydrochloric acid, but as lead is attacked under these conditions, the saturator must be constructed of stoneware or similar material, which has many disadvantages. It is now usually made by neutralising hydrochloric acid with concentrated gas liquor, and evaporating and crystallising the resulting solution, or by evaporating a solution of ammonium sulphate and sodium chloride in equivalent proportions; the sodium sulphate formed separates out during concentration as the monohydrate, which is removed by 'fishing,' leaving finally a concentrated solution of ammonium chloride, which is purified by crystallisation.

It is also manufactured by neutralising "galvanisers' pickle" (which consists chiefly of ferrous chloride) with ammonia, and by the action of ammonium carbonate (or of ammonia and carbon dioxide) on calcium chloride solution, the latter being obtained in large quantity as a by-product in the ammonia-soda manufacture, and in that of potassium chlorate; the solutions, of ammonium chloride obtained in either case

are evaporated and crystallised after removal of the precipitated substances.

Ammonium chloride is frequently further purified by sublimation, the sublimed product being known as *sal-ammoniac*. In this country the operation is carried out in large iron pots externally heated and covered with a similar concave iron plate on which the sublimate (sal-ammoniac) forms. This is detached at the end of the operation, the surface adhering to the iron, which is always discoloured, being removed previous to sale. In France the discolouration with iron is avoided by using earthenware pots, but the product is more expensive, owing to the fact that the pots are destroyed at each operation.

The commercial crystallised salt is white or only slightly discoloured, whilst the sublimed material has a fibrous structure, and frequently contains small amounts of iron. It is employed in pharmacy, soldering, galvanising, dyeing, and calico-printing, and in small quantities for many other purposes.

Ammonium Carbonate (Sal-Volatile).—The commercial product sold under this name consists of a mixture of ammonium bicarbonate $NH_4 \cdot HCO_3$ with ammonium carbamate $NH_2 \cdot CO \cdot ONH_4$, and contains about 31 p.c. of ammonia and 56 p.c. of carbon dioxide. It is usually prepared by subliming a mixture of about 1 part of ammonium sulphate with 1·5 to 2 parts of chalk in retorts, the evolved gases being passed into leaden chambers, where the carbonate is deposited as crusts on the walls, the exit gases being washed with water or sulphuric acid to recover the uncondensed ammonia. Lunge recommends the passing of an additional quantity of carbon dioxide through the chambers to effect a more complete recovery of the ammonia. As soon as the crust has attained a sufficient thickness it is detached, and is usually purified by resublimation. In Kunheim's process, the carbonate is prepared by passing ammonia obtained by the distillation of gas liquor direct into chambers, where it mixes with carbon dioxide and deposits the carbonate as a crust. (*See also* Bueb, Eng. Pat. 9177, 1910.)

The commercial product forms crystalline crusts, smelling strongly of ammonia, which is partially evolved on exposure to the air, the mass effloresces and leaving a powder consisting of ammonium bicarbonate. It is employed in wool-scouring, dyeing, and as a constituent of baking powders.

Ammonium Nitrate.—This salt is produced to a considerable extent for use in the explosive industry and in the preparation of nitrous oxide. It may be obtained by neutralising caustic ammonia with nitric acid, and evaporating and crystallising the solution if necessary, or by heating a mixture of ammonium sulphate and sodium nitrate in equivalent proportions, either alone or in solution. When the solution is concentrated, sodium sulphate separates out first for the most part, but the ammonium nitrate obtained simply by further evaporation is far from pure. According to Wedekind and Co. (Eng. Pat. 19465, 1906); a pure salt may be produced by a modified system of evaporation, of which the following example is given. A mixture of 400 parts of ammonium sulphate and 720 parts of sodium nitrate (40 p.c. excess) is dissolved in 900 parts of water, and the bulk of the sodium sulphate formed separated by evaporation. The filtered liquor is further concentrated till a sample on cooling to 70° deposits ammonium nitrate; the whole solution is then cooled to slightly above 70°, and after removal of the copious deposit of crystals of sodium nitrate and sulphate, the mother liquor is mixed with sufficient water to prevent the separation of sodium salts at 15°, 14 parts of water per 100 of mother liquor being sufficient with the above quantities. On then cooling to 15°, about 40 p.c. of the ammonium nitrate separates in the pure state. The mother liquor from these crystals, and the sodium nitrate previously separated, are employed in working up a further amount of ammonium sulphate.

The nitrate is also manufactured from the calcium nitrate now commercially prepared from the oxides of nitrogen obtained by the oxidation of atmospheric nitrogen, by heating it with a solution of rather less than an equivalent quantity of ammonium sulphate. Under proper conditions the reaction is said to be almost quantitative, the calcium sulphate separating in a readily removable form (Wedekind & Co. Eng. Pat. 20907, 1909). Attempts to obtain the nitrate from the calcium salt by the action of ammonia and carbon dioxide have not hitherto proved successful, owing to the formation of double salts.

Ammonium phosphate. Monammonium phosphate $(NH_4)H_2PO_4$, and diammonium phosphate $(NH_4)_2HPO_4$ have become commercial products by the process of Lagrange, which starts from commercial calcium superphosphate. This is lixiviated by water and steam, and a solution of 42°Tw. is obtained, together with a residue of calcium sulphate. Some of the latter remains in the solution, and is removed by carefully adding barium carbonate. The filtrate is neutralised by ammonia in slight excess, whereby all the lime is precipitated as basic phosphate, which is washed and used over again for the manufacture of superphosphate. The filtered solution, marking 32°Tw., contains monammonium phosphate, and can be worked for this or for diammonium phosphate. The latter is obtained by gradually mixing the above solution with *liquor ammoniæ* of sp.gr. 0·92, in the proportion of $1\frac{1}{2}$ equivalents of NH_3 to 1 of $(NH_4)H_2(PO_4)$. The diammonium phosphate at once separates out as a crystalline mass, which, after cooling, is submitted to hydraulic pressure. The operation is carried out in a closed vessel, to prevent the escape of ammonia. The mother liquor is employed for the manufacture of ammonia. The diammonium phosphate is principally used in Lagrange's sugar-refining process.

Ammonium thiocyanate is manufactured in considerable quantity in the crude state, but the product is for the most part simply employed as an intermediate product in the manufacture of cyanides. It occurs, as has been mentioned, in considerable amount in gas-liquor, and also in spent oxide, from which it may be extracted by water, but in both cases it is mixed with so many other impurities that its recovery is not remunerative; it may, however, be easily isolated as cuprous thiocyanate by precipitation

with copper sulphate and sulphurous acid. It is prepared synthetically from carbon disulphide by absorbing the latter in ammonia in presence of bases such as lime (Albright and Hood, Eng. Pat. 14154, 1894), the ammonium thiocarbonate first produced undergoing conversion into thiocyanate. A concentrated solution of ammonium thiocyanate is now prepared in a number of gas works, according to the British Cyanide Co.'s process (Eng. Pat. 13653, 1901), by passing the crude gas containing ammonia and hydrocyanic acid through a washer containing water and fed with powdered sulphur, the ammonium polysulphide first formed combining with the hydrocyanic acid to form thiocyanate, solutions of 30–50 p.c. strength being readily obtained, which only contain small amounts of other non-volatile ammonium salts.

The pure salt is used in dyeing and calico-printing, and may be obtained from the crude product by first converting it into the barium salt with baryta-water; or the barium salt may be produced by the action of barium sulphide on cuprous thiocyanate. After purification by recrystallisation, the barium salt is exactly precipitated with ammonium sulphate, and the solution evaporated and crystallised. The white deliquescent salt has frequently a reddish colour, due to the formation of the red ferric thiocyanate, from traces of iron present.

Ammonium persulphate. This salt is now produced on the commercial scale by the electrolysis of ammonium sulphate, and is employed for photographic purposes and as an oxidising agent. The commercial product usually contains small quantities of lead derived from the electrodes used in its manufacture.

H. G. C.

AMMONIACUM, AFRICAN, *v.* GUM RESINS.

AMMONIACUM, GUM, *v.* GUM RESINS.

AMMONIACUM, PERSIAN, *v.* GUM RESINS.

AMMONITE *v.* EXPLOSIVES.

AMMONIUM MELEQUETA *v.* COCCULUS INDICUS.

AMRAD-GUM. This gum forms white, yellow, and brown lumps of a sweetish taste and resinous smell. An aqueous solution (1 : 2) is viscid and strongly adhesive. It also gives with oil excellent emulsions, which keep very well. The dry substance contains 5·61 p.c. of ash, consisting of carbonic acid, lime, iron, magnesia, traces of phosphoric acid and silica. Has been recommended as a substitute for gum arabic. It was brought into the market some years ago, and comes from the Abyssinian highlands; is probably obtained from *Acacia elbaica* (Schweinfurth). (H. Unger and Kempf. Pharm. Zeit. 33, 218; J. Soc. Chem. Ind. vii. 446.)

AMYGDALASE, AMYGDALIN *v.* GLUCOSIDES.

AMYGDONITRILE GLUCOSIDE *v.* GLUCOSIDES.

AMYGDOPHENIN *v.* SYNTHETIC DRUGS.

AMYL ACETATE *v.* ACETIC ACID.

AMYL ALCOHOL $C_5H_{12}O$. The ordinary amyl alcohol (fusel oil, fermentation amyl alcohol, or *iso*amyl alcohol *Cl*-hydroxy-3-methyl butane) is one of the eight alcohols of the formula $C_5H_{12}O$ theoretically possible, and is the chief constituent of the fusel oil or 'last runnings' obtained in the rectification of alcohol, particularly of the alcohol made by the fermentation of potatoes. Amyl alcohol is a constituent of the product obtained when ordinary alcohol is formed by fermentation. The alcohol is got from the 'last runnings' by shaking the crude product with hot milk of time, decanting, drying over calcium chloride, and rectifying at a temperature of 132°. Pure amyl alcohol is obtained by preparing potassium amyl sulphate, purifying this by solution in alcohol and precipitation with ether, and subsequently decomposing by heating for five hours with 10 p.c. sulphuric acid.

Properties.—Amyl alcohol is a colourless liquid with a peculiar cough-exciting odour and a burning taste; it burns with a white smoky flame; b.p. 131·6° (corr.) and sp.gr. 0·8248 at 0°; 0·8113 at 18·7° (Kopp, Annalen, 94, 289); b.p. 128·9°–129·2° at 740·9 mm., and sp.gr. 0·8104 at 20°/4° (Brühl, Annalen, 203, 23); b.p. 130·5°–131° at 759·2 mm. (Schiff, Annalen, 220, 102). It is soluble in ethyl alcohol or ether, but is soluble in water only to the extent of 1 in 39 at 16·5° (Wittstein, J. 1862, 408), and 1 in 50 at 13°–14°, and the solution becomes milky at 50° (Balbiano, Ber. 1876, 1437). Amyl alcohol dissolves in all proportions in acetic acid diluted with an equal bulk of water (Berthelot and St. Gilles, J. 1862, 408). When oxidised with platinum black, ordinary valeric (*iso*valeric) acid is formed, whilst distillation with either manganese dioxide or potassium dichromate and sulphuric acid converts it into *iso*valeraldehyde and *iso*valeric acid. Sulphuric acid dissolves it in the cold, forming amyl-sulphuric acid, which, on heating, decomposes into amylene and its polymerides diamylene and tetramylene; these hydrocarbons, together with hexylene and the corresponding paraffins, are also obtained when amyl alcohol is distilled with zinc chloride (Wurtz, Annalen, 128, 316): it is probable, however, that the latter owe their formation to impurities in the alcohol. The action of chlorine has been studied by Barth (Annalen, 119, 216), and that of bleaching powder by Goldberg (J. pr. Chem. [2] 24, 116). The bromide (Cahours, Annalen, 30, 298; Balbiano, J. 1876, 348), chloride (Cahours, Annalen, 37, 164; Balard, Annalen, 52, 312; Balbiano, *l.c.*), and iodide (Cahours, Annalen, 30, 297) have been prepared by the action of the corresponding phosphorus compounds. Commercial amyl alcohol is generally lævorotatory; the degree of rotation, however, is not constant, but varies in different specimens, and the variation has been shown by Pasteur (Annalen, 96, 255) to be due to the fact that ordinary amyl alcohol is a mixture, in varying proportions, of two isomerides, one of which is optically inactive, and the other lævorotatory. When ordinary amyl alcohol is treated with sulphuric acid and the resulting amyl sulphuric acids converted into barium salts by neutralisation with barium carbonate, a separation of the two isomeric alcohols can be effected, inasmuch as the barium salt of the optically active alcohol is 2½ times more soluble in water than the corresponding salt of the optically inactive modification. (For an examination of the properties and physical constants of commercial amyl alcohol, *see* Richmond and O'Shaughnessy, J. Soc. Chem. Ind. 1899, 107.) Marckwald and McKenzie have reviewed the previous work of

Ley, Le Bel, Bakhoren, and Chapman. They have succeeded in dividing the commercial alcohol into its constituents by fractional crystallisation of their nitrophthalic esters, and find that active amyl alcohol has $[\alpha]_D$ −5·90° at 20°. The other constituent is *iso*butyl carbinol (Ber. 1901, 485, 479; 1909, 1583).

Amyl alcohol has been used as a solvent for nitrocellulose in the manufacture of celluloid, as have also its chlorination products Liebert has utilised amyl nitrate (D. R. P. 51022) by adding it to nitroglycerine in order to diminish its sensitiveness to cold and concussion.

In addition to the optically active and inactive modifications obtained from ordinary amyl alcohol, the following isomeric alcohols have been prepared:—*Normal amyl alcohol* (Lieben and Rossi, Annalen, 159, 70; Schorlemmer, Annalen, 161, 268); *methylpropyl carbinol* (Schorlemmer, *l.c.*; Saytzew and Wagner, Annalen, 175, 351; 179, 313; Markownikow, J. 1883, 861); *methylisopropyl carbinol* (Wyschnegradsky, *l.c.*; Münch, Annalen, 180, 339; Winagradow, Annalen, 191, 125); *diethyl carbinol* (Saytzew and Wagner, *l.c.*); *dimethylethyl carbinol* (Wurtz, Annalen, 125, 114; 127, 236; 129, 365; Berthelot, Annalen, 127, 69; Flavitzky, Annalen, 179, 348; Wyschnegradsky, *l.c.*; Osipoff, Ber. 1875, 1240).

AMYL NITRITES $C_5H_{11}NO_2$. **Commercial amyl nitrite** is a mixture of the nitrites of *iso*butyl carbinol and active amyl alcohol

$$(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot NO_2 + CH_3(C_2H_5)CH\cdot CH_2\cdot NO_2$$

It may also contain *iso*butyl nitrite, and always contains some unaltered amyl alcohol. Curtmann (J. Soc. Chem. Ind. 1893, 372) gives examples of specimens containing from 33 p.c. to 93 p.c. of amyl nitrite. It is prepared by passing nitrous fumes into amyl alcohol (Balard, Ann. Chim. Phys. [3] 12, 318; Williams and Smith, Pharm. J. 1886, 499); by distilling together the theoretical quantities of amyl alcohol and potassium nitrite with excess of dilute sulphuric acid; or by passing nitrosyl chloride into a mixture of equimolecular proportions of dry pyridine and amyl alcohol (Bouveault and Wahl, Compt. rend. 136, 1563). The last is a general method for the preparation of nitrous esters, and gives a yield of 80 p.c. in the case of amyl nitrite. The commercial article is a yellow liquid with characteristic odour, which should boil between 97° and 99°, and have a sp.gr. 0·870 to 0·880. It is of value as a stimulant in angina pectoris and similar affections.

Normal amyl nitrite $CH_3\cdot(CH_2)_3\cdot CH_2NO_2$ is a pale-yellow liquid, boiling at 104°; sp.gr. 0·8528 at 20°. The nitrite group is readily removed by dilute potash (Marcel Pexsters, Chem. Zentr. 1907, i. 1398).

Isobutyl carbinol nitrite

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\cdot CH_2\cdot CH_2\cdot NO_2$$

from pure *iso*butyl carbinol, boils at 97°, and has sp.gr. 0·880 (Dunstan and Williams, Pharm. J. 1889, 487).

Tertiary amyl nitrite $(CH_3)_2(C_2H_5)C\cdot NO_2$ (Bertoni's amylonitrous ether) has been used as a substitute for ordinary amyl nitrite, its action being stronger in degree and more lasting. It is a yellow liquid with weak camphoraceous odour, tasting like peppermint. It boils at 93°. (J. Soc. Chem. Ind. 1889, 1003).

AMYLACETIC ACID (Active) *v.* HEPTOIC ACIDS.

***iso*-AMYLACETIC ACID** *v.* HEPTOIC ACIDS.

α- and β-AMYLANS $n(C_6H_{10}O_5)$?

After first extracting cereals with strong alcohol, the aqueous extract contains gummy lævorotatory colloidal carbohydrates, which are precipitated by strong alcohol. The product so obtained from barley is a mixture, part being soluble in cold water. The insoluble crumbly residue, amounting to 2 p.c. of the barley, is α-amylan. It has $[\alpha]_D$ −21·6, and does not reduce Fehling's solution; it is gelatinised in hot water, and yields viscous solutions even at 1–2 p.c. concentration. O'Sullivan (Chem. Soc. Trans. 1882, 41, 24) found it to be present in barley, oats, wheat, and rye, especially in the two first named. The soluble product β-amylan has $[\alpha]_D$ −65°; it amounts to 0·3 p.c., and is very similar to α-amylan in properties.

O'Sullivan obtained from β-amylan, by fractional precipitation with alcohol or on boiling with milk of lime, a similar substance $[\alpha]_D$ −129·7°. This he regarded as a decomposition product, but this is probably not the case. O'Sullivan states that the amylans yield glucose alone on hydrolysis. Lintner and Düll (Zeit. angew. Chem. 1891, 538) obtained galactose and xylose from barley gum. Wroblewski (Ber. 1893, 30, 2289) obtained arabinose. Lindet (Berlin Congress, 1903, 3, 498) isolated a dextrorotatory gum from barley, in addition to a lævo-rotatory gum.

Contrary to O'Sullivan's statement that diastase is without action on amylan, Horace Brown (Trans. Guinness Research Laboratory, 1906, 317, where there is a full account of amylan) finds that when barley gum is steeped in malt extract it swells up and undergoes gradual liquefaction and solution, and in a few days its colloidal nature is lost. This is one of the most significant changes which mark the conversion of barley into malt.

To prepare 'amylans' in quantity, Brown boils the finely divided grain with water, treats with malt extract at 50°–55° for an hour to liquefy the starch, boils again, and filters. The filtrate is concentrated in vacuum to sp.gr. 1·060, and three volumes 80 p.c. alcohol (by volume) added gradually. The crude amylans are precipitated in large white flocks free from dextrin and have no cupric reducing power. Corrected for ash and nitrogen they amount on a number of dry barleys to about 9·6 p.c., and have $[\alpha]_D$ +62° to +73°. This amount practically accounts for the whole of the missing constituents of the soluble portion of barley after hydrolysis with malt extract.

On hydrolysis about 60 p.c. of glucose is formed, together with arabinose, xylose, and an unknown substance of low angle and reducing power.

The above dextrorotatory amylan represents everything insoluble in 62 p.c. alcohol. By a variation of the method of preparation a carbohydrate $[\alpha]_D$ −100·34°, corresponding to Wroblewski's araban, was obtained.

It is obvious that the 'amylans' require further investigation. According to O'Sullivan, it is probably owing to the presence of amylan

that unmalted barley cannot be satisfactorily employed in the preparation of beer. Malted grain does not contain it. Distillers using raw grain (oats and barley) have at times much difficulty in separating the wort (solution of sugars, &c.) from the grains (undissolved portion of the grain employed) in consequence of the presence of amylan in quantity, the barleys and oats of some seasons containing much more of it than at other times. E. F. A.

AMYLASE *v.* DIASTASE; *also* ENZYMES.

AMYLENE C_5H_{10}. Eight isomeric amylènes are theoretically possible, and all have been prepared. These hydrocarbons have been chiefly studied by Flavitzky (Annalen, 179, 340), Wyschnegradsky (Annalen, 190, 336), and by Kondakoff (J. Russ. Phys. Chem. Soc. 24, 381), and can be obtained by the action of alcoholic potash on the various amyl iodides; or by the action of dehydrating agents such as sulphuric acid or zinc chloride on amyl alcohol. They can often be converted into one another by the action of hydriodic acid and the subsequent removal of the latter, thus:

$$Me_2CH{\cdot}CH:CH_2+HI \rightarrow Me_2CH{\cdot}CHIMe \xrightarrow[+\text{alcohol}]{KOH} Me_2C:CHMe.$$

The amylene ordinarily met with is trimethylethylene, and is chiefly obtained by the dehydrating action of zinc chloride on fermentation amyl alcohol.

Preparation.—To prepare amylene, fermentation amyl alcohol (1 part) is shaken with coarsely powdered zinc chloride (1½ parts), allowed to remain for twenty-four hours, and then distilled. The product consists of a complex mixture of paraffins from C_5H_{12} to $C_{10}H_{22}$ with olefines from C_5H_{10} to $C_{10}H_{20}$ (Wurtz, J. 1863, 507). These can be isolated by fractional distillation (Wurtz), but according to Eltekow (J. Russ. Chem. Soc. 14, 379), amylene is most readily obtained if the product is well cooled, and shaken with dilute sulphuric acid (2 vols. of acid to 1 vol. of water), the acid layer separated, diluted with water, and distilled; the distillate consists of amylene (trimethylethylene) and tertiary amyl alcohol, and the latter, on distillation with sulphuric acid (1 : 1), yields pure trimethylethylene. Pure trimethylethylene can be prepared by heating tertiary amyl iodide Me_2ClEt with alcoholic potash (J. Russ. Phys. Chem. Soc. 17, 294). It can also be formed by dropping tertiary amyl alcohol on to oxalic acid (D. R. P. 66866).

Other methods for obtaining ordinary amylene have been described by Balard (Ann. Chim. Phys. [3] 12, 320); Bauer (J. 1861, 659), and Linnemann (Annalen, 143, 350); Kondakoff (*l.c.*); Ipatieff (J. Russ. Phys. Chem. Soc. 30, 292); Tornöe (Ber. 21, 1282); Blaise and Courlot (Bull. Soc. chim. 35, 582).

Properties.—Amylene is a colourless liquid, b.p. 36°–38° and sp.gr. 0·6783 at 0° (Le Bel, Bull. Soc. chim. 25, 547); b.p. 36·8° at 752·7 mm. (Schiff, Annalen, 223, 65). It combines directly with a large number of substances: with nitric peroxide (Guthrie, Chem. Soc. Trans. 13, 129; Wallach, Annalen, 241, 291; 248, 161; Miller, Chem. Soc. Proc. 3, 108; Demganoff, Chem. Zentr. 1899, i. 1064); sulphur chloride and chlorine (Guthrie, Chem. Soc. Trans. 12, 112; 13, 45, 129; 14, 136; Kondakoff, J. Russ. Phys. Chem. Soc. 20, 141; 24, 381; Ber. 24, 929; Hell and Wildermann, *ibid.* 216); with bromine (Wurtz, Ann. Chim. Phys. [3] 55, 458; Hell and Wildermann, *l.c.*; Kondakoff, *l.c.*), and, when cautiously mixed with well-cooled sulphuric acid, sp.gr. 1·67 (2 vols. H_2SO_4 to 1 vol. water), in a freezing mixture, is converted into dimethylethyl carbinol, b.p. 101·6°–102°/762·2 mm., which has valuable hypnotic properties (J. Soc. Chem. Ind. 8, 1002; 9, 650, 889), and can be obtained, after neutralisation with sodium hydroxide; on distillation (Flavitzky, 175, 157) with sulphuric acid, sp.gr. 1·545 (2 pts. by weight H_2SO_4 to 1 pt. water), methyl*iso*propyl carbinol is obtained (Osipoff, Ber. 8, 542, 1240). Amylene forms compounds with metallic salts (Denigès, Compt. rend. 126, 1146; Kondakoff, J. Russ. Phys. Chem. Soc. 25, 35). When heated to high temperatures, benzene, naphthalene, acetylene, methane, carbon, and hydrogen are produced, the products depending on the temperature (Haber and Oechelhäuser (Chem. Zentr. 1897, i. 225). The action of nitrosyl chloride on amylene has been studied by Tilden and Sudborough (Chem. Soc. Trans. 1893, 482).

In addition to ordinary amylene, the following isomerides have been obtained:—*Normal amylene*, b.p. 39°–40° (Wurtz, Annalen, 123, 205; 127, 55; 148, 131; Zeidler, Annalen, 197, 253; Kondakoff, J. Russ. Phys. Chem. Soc. 24, 113; Flavitzky and Wyschnegradsky, *l.c.*); *isopropylethylene*, b.p. 21·1°–21·3° (Flavitzky and Wyschnegradsky, *l.c.*; Kondakoff, *l.c.*; Ipatieff, *l.c.*); *symmetrical methylethylethylene*, b.p. 36° at 740·8 mm. (Wagner and Saytzew, Annalen, 175, 373; 179, 302; Kondakoff, *l.c.*; Lissier, Bull. Soc. chim. 9, (3) 100); and *unsymmetrical methylethylethylene*, b.p. 31°–32°, sp.gr. 0·67 at 0° (Wyschnegradsky, *l.c.*; Le Bel, Bull. Soc. chim. 25, 546; Kondakoff, *l.c.* 25, 354); *Methyltetramethylene*, b.p. 39°–42° (Coleman and Perkin, Chem. Soc. Trans. 1888, 201); *pentamethylene*, b.p. 35° (Gustavson and Demganoff, J. Russ. Phys. Chem. Soc. 21, 344; Markownikoff, Ber. 30, 975; Young, Chem. Soc. Trans. 1898, 906; Wislicenus and Hanschel, Annalen, 275, 327); and *dimethyltrimethylene* (Gustavson and Popper, J. pr. Chem. 166, 458).

The action of hydrogen iodide on the amylenes has been investigated by Saytzew (Annalen, 179, 126); whilst Zeidler (Annalen, 186, 245) has examined the products obtained when various amylenes are oxidised with potassium permanganate in acid, neutral and alkaline solution, with chromic acid, and with potassium dichromate and sulphuric acid. The halogen derivatives of the various amylenes have been investigated (Lipp, Ber. 22, 2572; Hell and Wildermann, 23, 3210; Ipatieff, J. pr. Chem. 161, 257; Chem. Zentr. 1898, ii. 472; Brochet, Ann. Chim. Phys. 1897, 10, 381; Wassileef, Chem. Zentr. 1899, i. 775; Froebe and Hochstetter, Monatsh. 23, 1075; Kukuritschkin, J. Russ. Phys. Chem. Soc. 35, 873; Schmidt and Leipprand, Ber. 37, 532; Hamonet, Compt. rend. 138, 1609). Also the action of oxalic acid on various amylenes (Miklosheffsky, J. Russ. Phys. Chem. Soc. 22, 495), the nitrolamines (Wallach and Wohl, Annalen, 262, 324), and the nitrosites and nitrosates (Ipatieff, Chem. Zentr. 1899, ii. 178; Schmidt, Ber. 35, 2323, 2336, 3737; Hantzsch,

2978, 4120; Schmidt and Austin, Ber. 36, 1768).

The following polymerides of amylene have also been obtained, and can be prepared by heating ordinary amyl alcohol or amylene with zinc chloride:—*Diamylene* $C_{10}H_{20}$, b.p. 157°–157·5°/759 mm. (Balard, Annalen, 52, 316; Schneider, Annalen, 157, 207; Bauer, Jahresbericht. 1861, 660; Kondakoff, J. pr. Chem. 162, 442; Gasselin, Ann. Chim. Phys. 1894, 3, 5); *triamylene* $C_{15}H_{30}$ (Bauer, *l.c.*; Gasselin, *l.c.*); and *tetramylene* $C_{20}H_{40}$ (Bauer, *l.c.*). Also derivatives of diamylene (Schindelmeister, Chem. Zentr. 1896, ii. 354).

AMYLOCARBOL. Trade name for a disinfectant, said to consist of carbolic acid 9 pts., amyl alcohol 160 pts., green soap 150 pts., water 690 pts.

AMYLOCOGULASE *v. Enzymes*, art. FERMENTATION.

AMYLOFORM. An antiseptic prepared by the action of formic aldehyde upon starch (Claassen, Pharm. Zeit. 41, 625) (*v.* SYNTHETIC DRUGS).

AMYRIN *v.* OLEO-RESINS.

ANACAHUITA. A wood of unknown botanical origin imported from Mexico; its preparations are said to be useful in pulmonary disorders. The wood contains a volatile oil, an iron-greening tannin, gallic acid, a yellowish resin, sugar, a tasteless volatile body crystallising in warty masses, and a bitter substance crystallising in white needles (J. 1861, 771).

ANACARDIUM NUT (Cashew Nut, Kajoo) is the fruit of *Anacardium occidentale* (Linn.), a tree indigenous to Brazil, Central America, and the West Indies. It has been transplanted to, and become naturalised in, many parts of India. The fruit rests on a fleshy edible peduncle, from which a spirit is distilled in Mozambique and in Western India. The nut is edible after it has been roasted to expel the cardol which it contains; the cardol thus obtained is used at Goa for tarring boats, and as a preservative of woodwork (Dymock, Pharm. J. [3] 7, 730). In addition to cardol, the nuts contain anacardic acid, and an oily matter which, by exposure to the air, assumes a fine black colour, permanent against acids, alkalis, chlorine, and hydrocyanic acid. It has been recommended as a marking ink, and is used for giving a black colour to candles (Böttger, Dingl. poly. J. 205, 490). From the stem of the plant a gum exudes which is said to be used by book-binders in South America.

The kernels contain 47·2 p.c. of a fatty oil, having the following characteristics:—Saponification value, 187; iodine value, 77–83·6; refraction in Zeiss' butyro-refractometer at 25°, 58·1–58·8 (Theopold, Pharm. Zeit. 1909, 1057).

J. L.

ANÆSTHETICS. There are three principal types of anæsthesia, or loss of sensation sufficient to allow of surgical operations without pain. In *local* anæsthesia the actual tissues to be lacerated are infiltrated with some substance which paralyses the endings of the nerves that convey painful sensations. In *general* anæsthesia, total insensibility and loss of muscular power are produced by the action of drugs on the brain, carried there in the circulation; extensive operations on any part of the body can then be done. In *spinal* anæsthesia, the whole of the nerves supplying large sections of the body are paralysed at their exit from the spinal cord by applying to the latter a drug which is injected into the vertebral canal. Thus spinal anæsthesia resembles general anæsthesia inasmuch as it causes loss of sensation and muscular power together over a wide region, and local anæsthesia in that consciousness is not lost and the anæsthetic is not diffused in the circulation.

Local anæsthetics. Very little is known of the action of these on the tissues with which they come in contact. They are all protoplasmic poisons which have a special preferential action upon nervous structures. Those in common use are: cocaine, stovaine, novocain, tropacocaine, β-eucaine, alypin, β-eucaine lactate, nirvanine, holocaine hydrochloride, acoine, orthoform, anæsthesine. Braun has formulated postulates for appraising local anæsthetics. Omitting one which has not secured general assent, they are:

(1) Low toxicity in proportion to local anæsthetising power.

(2) Solubility in water to 2 p.c. at least; and stability of the solution, which should keep without deteriorating and be capable of sterilisation by boiling.

(3) Non-irritability to the tissues, and freedom from after-effects when absorbed into the circulation.

(4) Compatibility with adrenalin.

Acoine, holocaine hydrochloride, anæsthesine, and orthoform are more or less insoluble. β-eucaine is about on the 2 p.c. border line. The others are freely soluble and will keep without deteriorating. Cocaine solutions cannot be boiled, but stovaine, novocain, β-eucaine lactate, tropacocaine, alypin, and nirvanine can be thus sterilised, at 115° if necessary.

The most powerful anæsthetic action is that of stovaine. Next are cocaine, novocain, tropacocaine, alypin, and β-eucaine lactate, which are all about equal. The others have inferior actions in this respect. Experiments on mice and rabbits have resulted in the following table of relative toxicity, cocaine being taken as the unit[1]:—

Alypin, 1·25	Stovaine, 0·625
Cocaine, 1·00	Novocain, 0·490
Nirvanine, 0·714	β-eucaine lactate, 0·414

The irritant action of stovaine, tropacocaine, and β-eucaine lactate is greater than that of cocaine; that of novocain is less. All these five are compatible with adrenalin if the solutions are fresh mixed for each case. They are extensively employed; but novocain is evidently the best yet discovered for routine use.

Local anæsthetics are used dissolved in water or in normal saline solution. It is not essential that they should be injected subcutaneously; where the surface tissues are delicate, as on the eye, larynx, tongue, tonsils, simple contact with a local anæsthetic in solution or in fine powder will destroy sensation sufficiently for many surgical procedures. But elsewhere the solution is injected with a hypodermic syringe into the tissues which are to be rendered anæsthetic. If adrenalin be mixed with the anæsthetic solution, contraction of all the minute blood-vessels in the locality takes place.

[1] Le Brocq, Pharm. J. 1909, 674.

Thus the drug is retained longer in the tissues about the site of injection, instead of being rapidly dissipated in the blood-stream. Consequently a more intense and lasting, because more strictly local, action occurs.

Local anæsthesia can also be obtained by freezing the superficial tissues. A fine jet of ether or ethyl chloride is directed on to the desired portion of the skin, and when the latter is frozen a cut can be made, as for a whitlow, boil, or other small abscess, without causing pain.

Spinal anæsthetics. Some of the same drugs which cause local anæsthesia are available for injection into the cerebro-spinal fluid with which the spinal cord is surrounded in the vertebral canal. Stovaine and novocain are most used in Britain, but tropacocaine also is popular in Europe. The method was introduced by Bier in Germany in 1899, and since 1907 has been very extensively tried all over the world. The balance of opinion is that for ordinary cases spinal anæsthesia is too dangerous to replace general anæsthesia; but that for certain cases where the latter entails especial risks, it is of undoubted utility. Barker[1] and McGavin,[2] who are the most prominent advocates of spinal anæsthesia in England, use a solution of stovaine in 5 p.c. glucose; 4 to 7 centigrammes of stovaine is the dose for an adult. Ryall, following Jonnesco of Bucharest, adds half to one milligramme of strychnine to 4 to 10 centigrammes of novocain.[3] Strychnine is also used with stovaine, and with tropacocaine; the object is to prevent the anæsthetic from causing death if it should by any chance reach the respiratory centre near the upper end of the spinal cord. Bier has used morphia with scopolamine (hyoscine) as a preliminary, injected hypodermically; but he seems now to be convinced that the method which he originated is too risky to replace general anæsthesia.[4]

General anæsthetics. There are many substances which diminish or abolish the perception of pain; but only a few of these are freely used as general anæsthetics. The conditions which must be fulfilled to obtain admission to the list are[5]:

(1) To produce absolute insensibility to pain without causing any great discomfort during induction.

(2) To produce loss of all voluntary and many reflex movements.

(3) To be capable of being readily introduced into the system, and rapidly eliminated, after the completion of the operation, without injury to the patient.

(4) To act in a regular and constant way, so that the effects can be controlled by the administrator.

The general anæsthetics in use in Great Britain are four in number: nitrous oxide, ethyl chloride, ether, chloroform. Ethyl bromide, ethidene dichloride (dichlorethane), bichloride of methylene, and amylene (pental) are obsolete. In America and on the Continent anæsthol, somnoform, and narcotile are also employed. Anæsthol is a mixture of chloroform, ether, and ethyl chloride, in molecular proportions; somnoform is ethyl chloride 60 parts, methyl chloride 35 parts, ethyl bromide 5 parts; narcotile has been stated to be a compound, but analysis has shown it to be a mixture of methyl chloride, ethyl chloride, and ether. Mixtures of ether and chloroform in various proportions are in common use everywhere. Morphine, chloral, cannabis indica, and many other drugs have analgesic and anæsthetic properties; some of them, morphine especially, are used to assist the action of the volatile anæsthetics.

The effects of a general anæsthetic are produced by the circulation in the blood of the drug employed. When it reaches the brain the phenomena of anæsthesia are exhibited: at first slightly, then with increasing doses more and more intensely, until with a sufficient quantity death results. The phenomena of general anæsthesia are the same whether absorption takes place through the lungs, rectum, skin, or gastro-intestinal tract. Thus alcohol has a marked anæsthetic effect, familiar in the indifference of a drunken man to injury.

The easiest way of introducing into the blood any substance which is a gas or a volatile liquid is by means of the lungs. The blood thus charged with an anæsthetic is rapidly delivered to the nervous centres, in which the essential changes of general anæsthesia take place. The absorption of vapours in the lungs varies with numerous factors: barometric pressure, temperature of the vapour and of the blood, rate of respiration, and rate of blood-flow through the pulmonary system. But the process is also something more than simple solution by diffusion of gases through a thin membrane; there is at least an element which depends on the fact that the tissues concerned are living.

The lungs are also the chief, but not the only, medium for the elimination of inhaled anæsthetics. These are but little decomposed during their tour of the circulation, and the greater part is discharged unchanged after the administration is suspended. What change they undergo in the blood is very uncertain. Chloroform, which has hitherto received more attention in this respect than the others, is recoverable from the blood in fatal cases of chloroform anæsthesia, but it is believed that most of it circulates in the red corpuscles of the blood in combination with the lecithin and cholesterin which they contain.[1] Glycuronic acid not uncommonly appears in the urine after chloroform anæsthesia. Nitrogen and sulphur are also excreted in the urine in greater quantity, indicating a greater destruction of proteid; and the increase of chlorides is held to show that some chloroform is decomposed in the body. The affinity of cholesterin and lecithin for chloroform, chloral, ether, sulphonal, tetronal, trional, and chloralamide has been suggested as the explanation for the selective action of these narcotics on the central nervous system, which contains a larger proportion of cholesterin and lecithin than do the other organs. With regard to ether, Turnbull states that etherisation

[1] British Medical Journal, 1908, ii. 453 (and other papers).
[2] Practitioner, August, 1909; British Medical Journal, Sept. 17, 1910.
[3] Clinical Journal, July 17, 1909.
[4] Deutsch. Zeitschr. f. Chirurgerie, xcv. 373.
[5] R. W. Collum, The Practice of Anæsthetics, 1909, 14.

[1] Hale White, Materia Medica, 11th ed. 1909, 280.

produces a marked diminution of the hæmoglobin of the blood [1]; and Reicher finds three times the normal quantity of fat present in the blood, together with an increased amount of acetone, due to the disintegration of fat and albuminoid bodies.[2] The chemical composition of the blood is often much modified during anæsthesia, because the air supply to the lungs is frequently curtailed to a greater or less extent, and the elimination of CO_2 hindered. The proportions of O and CO_2 in the circulating blood may thus be altered at the expense of the former, and an asphyxial element added to the narcotic effect of the anæsthetic. Some authorities believe that deprivation of oxygen is the method by which all anæsthetics produce their action on the nervous tissues.[3]

The chemical changes which may be assumed to take place in the brain during anæsthesia are unknown, as indeed are those of natural sleep. It has been suggested that unstable compounds are formed between the anæsthetic and the protoplasm of the nerve cells, and some observers describe changes recognisable microscopically in those cells as a result of anæsthesia. Professor Hans Meyer holds that there is a loose physico-chemical combination with the lipoids of the cell. This causes inhibition of the normal metabolism until the loose reversible combination breaks up. A rare sequel of chloroform anæsthesia is known as delayed chloroform poisoning. The symptoms of this condition, which is sometimes fatal, arise about eighteen to seventy-two hours after the anæsthesia. They are attributed to 'acidosis,' that is to diminished alkalinity of the blood due to the presence of acetone and aceto-acetic acid, which can be detected in the urine and the breath. For the developed condition sodium bicarbonate in large doses is employed; as a preventive measure feeding on glucose for a day or two before operation is found to answer best.[4] Very rarely indeed this acidosis has followed the administration of ether.

Nitrous oxide (Laughing gas).—The inhalation of from three or four to twenty or thirty gallons of this gas without any air produces anæsthesia. If the administration is then suspended, insensibility lasts on an average about thirty to forty-five seconds, during which time minor operations such as the extraction of teeth can be undertaken. A marked asphyxial element is nearly always present, owing to the replacement of oxygen by N_2O. If air be admitted for brief periods between successive doses of gas, anæsthesia can be maintained without great difficulty for several minutes. By delivering nitrous oxide mixed with pure oxygen for inhalation, anæsthesia can be prolonged for any desired period. The proportions of the two gases are varied to meet the requirements of individual cases, but roughly the mixture must contain about 80 p.c. by volume of N_2O. The previous injection of narcotics such as morphine, with atropine, facilitates the induction of anæsthesia. This method is well suited for operations on the limbs, but for abdominal operations it is difficult to get the complete muscular relaxation necessary. Nitrous oxide gas is the safest known general anæsthetic, and recovery takes place very rapidly (two or three minutes) without unpleasant after-effects.

Ethyl chloride.—The vapour of 3 to 5 c.c. of this substance allowed to volatilise in a closed chamber, such as a rubber bag, into which an adult patient exspires and from which he inspires, produces anæsthesia very rapidly. If administration is then suspended, insensibility lasts from one to two minutes. By administering a further dose before recovery takes place from the first one, anæsthesia can be prolonged; it is preferable, however, to give ether or chloroform or nitrous oxide and oxygen if a longer anæsthesia is required. The after-effects of ethyl chloride are intermediate between those of nitrous oxide and those of ether and chloroform. Ethyl chloride given by an expert is safer than either of the latter, but not so safe as nitrous oxide.

Ether.—About 30 p.c. of air and 70 p.c. of ethereal vapour will produce and maintain general anæsthesia. The vapour is so intensely irritating to the mucous membrane which lines the mouth, nose, and air-passages, that it must first be offered very dilute, and then in a gradually increasing percentage. Limitation of air supply renders it possible to procure anæsthesia with a much smaller quantity of ether than when fresh air is freely admitted, for a slight concurrent asphyxia helps the action of the ether. Such asphyxiation has disadvantages of its own if allowed to exceed a very moderate degree; it is usually present during anæsthesia under ether by the 'closed' methods. There is slightly more difficulty in producing anæsthesia by the 'open' method, in which air enters freely; the preliminary injection of small doses of morphine ($\frac{1}{8}$ to $\frac{1}{4}$ grain) with atropine ($\frac{1}{200}$ to $\frac{1}{100}$ grain) is of advantage. Ether is much less dangerous to life than chloroform in the operating room: but part of this advantage is counterbalanced by the occasional development of bronchitis and broncho-pneumonia afterwards.

Chloroform.—Much research has been carried out to determine the percentage of chloroform necessary to produce anæsthesia by inhalation. Vernon Harcourt introduced early this century a chloroform inhaler capable of regulating this proportion up to 2 p.c. Experience showed that in occasional cases it is very difficult or impossible to induce anæsthesia with this amount, and a modification of the instrument allows air to be inspired containing 3 p.c. In practically every case anæsthesia, when fully established, can be maintained with a 2 p.c. vapour. Alcock, who has investigated the dosage of chloroform very carefully, finds [1] that for an ordinary adult it suffices to offer a percentage rising gradually to $2\frac{1}{2}$ in three minutes; this as a rule produces complete surgical anæsthesia in eight to ten minutes. If a higher proportion is necessary, 3 p.c. may be allowed at the end of five minutes. He finds that within a few minutes after induction is complete 1·5 p.c., and after half an hour 1 p.c., will usually be enough. Several physiologists have estimated the amount of chloroform in the circulating blood during

[1] Laurence Turnbull, Artificial Anæsthesia, 223.
[2] Reicher, Lancet, Jan. 25, 1908, 268.
[3] R. Gill, The $CHCl_3$ Problem, 1906.
[4] Wallace and Gillespie, Lancet, Dec. 5, 1908, 1665.

[1] N. H. Alcock, British Medical Journal, Feb. 6, 1909, 325.

anæsthesia: their results vary from 0·035 to 0·07 p.c. Chloroform is the most dangerous of these four anæsthetics, especially in the hands of those whose experience as anæsthetists is small. H. R.

ANALGESINE. Identical with antipyrine (*q.v.*).

ANALYSIS. Chemical analysis is the separation of a complex material into simpler constituents. It is *ultimate* when these component parts are elementary forms of matter, and *proximate* when the subdivision consists only in the separation of the original substance into less complicated compounds. The aim of chemical analysis is twofold: the first object is to ascertain the nature of the components of a mixture or complex substance; the second is to determine the proportions in which these constituents are present. All analytical operations may therefore be classified under the two main categories of *qualitative* and *quantitative* analysis, according as to whether these processes lead to the identification of the proximate or ultimate constituents of a complex substance, or to the determination of the relative proportions in which these constituents are present.

This article is written primarily from the technical point of view, and accordingly the descriptions given in the qualitative section are restricted mainly to those elements which find application in the arts and industries. Similarly, the estimations and separations outlined in the quantitative section are chiefly those required in the analysis of technically important materials.

The systematic investigation of the individual elements and their typical compounds has revealed the existence of many characteristic reactions which are exhibited by certain elements and compounds under widely varying conditions of combination or association. This circumstance leads to a simplification which is utilised extensively in both qualitative and quantitative analysis. In qualitative work, such characteristic reactions as are not generally interfered with by other substances enable the analyst to detect the presence of certain elementary or compound substances without undertaking the more laborious processes involved in isolating these constituents from the other ingredients of a mixture.

In quantitative analysis two essentially different methods of procedure are employed, the more fundamental one being *gravimetric* analysis, in which the elementary or complex constituent of a mixture is isolated and weighed in the form of a definite compound. By utilising quantitatively the above-mentioned distinctive reactions it is frequently possible to adopt the second procedure known as *volumetric* analysis, in which the relative amount of a certain constituent is estimated in the presence of other elements and compounds associated with this constituent in the mixture under examination.

For the purposes of scientific investigation the most accurate methods are essential, and these are, in the main, gravimetric in character; but for technical requirements extreme accuracy is rarely required, and rapid methods giving approximately correct results are preferred to more exact processes involving a longer time for their execution. It is in this direction that volumetric analysis has been most extensively developed, the general tendency in industrial laboratories being to replace gravimetric methods by quicker volumetric processes with very little loss in accuracy, provided that certain essential conditions be fulfilled.

General Operations.

Sampling.—It is of the highest importance that the sample under examination should be truly representative of the bulk of the substance. Discrepancies between the results of different analysts are usually attributed to faulty methods or inaccurate work, but in many cases they are really due to imperfect sampling. If the substance is a liquid, the contents of the vessel should be thoroughly mixed before the sample is withdrawn. If the substance is contained in several vessels, a proportional quantity should be taken from each, the different portions mixed together, and the final sample taken from the mixture.

In the case of solid products care must be taken to secure a proper proportion of large and small, hard and soft fragments. If a ship's cargo is to be sampled, portions should be taken from different parts of the bulk; if the substance is contained in railway trucks, portions should be taken from the ends and middle of each truck. When the substance is in bags or barrels, a long hollow auger is thrust to the bottom of each and then withdrawn, bringing with it a long core of the substance. If the material loses or gains moisture, or undergoes any other change on exposure to air, as in the case of soap or caustic soda, a proper proportion of the internal and external portions must be taken. In all cases the first samples are broken into small pieces, thoroughly mixed, and one-fourth taken for further treatment. This is ground to powder, again thoroughly mixed, and one-fourth taken. The subdivision is repeated, if necessary, and the final sample kept in well-closed bottles. This process of 'quartering' may also be effected by spreading out the finely powdered material in the form of a flattened cylinder dividing this radially into four parts, taking out the opposite sectors, mixing these thoroughly, and repeating the subdivision.

If the mixture is soft and friable, pulverisation is readily effected in a porcelain or earthenware mortar, but harder substances should be powdered in a cast-iron or steel mortar. When the substance is hard, and a very fine powder is required, an agate mortar should be used for the final operation, so that the powder may be completely sifted through fine muslin. Very hard substances, such as minerals, are first broken into small pieces by wrapping them in paper and striking with a hammer, and are then further crushed in a steel mortar (Fig. 1) consisting of a strong base with a circular recess into which fits a movable steel ring or guard, and inside this is a solid steel piston which acts as a pestle. A small quantity of the mineral is placed on the base of the mortar inside the guard-ring, the

FIG. 1.

latter is held firmly down, and the piston is placed inside and struck smartly with a hammer, which drives it down upon the mineral. The final crushing is done in an agate mortar.

The mechanical ore-grinder described in Hillebrand's Analysis of Silicate and Carbonate Rocks, may likewise be employed in reducing hard minerals to a fine powder.

Drying.—Many substances absorb more or less moisture when exposed to the air, and in order to bring them into a definite condition for analysis, it is desirable that they should be dried, this operation being conducted at the ordinary or at a higher temperature according to circumstances. Substances which contain water in combination are usually dried by exposure to air or by pressure between folds of filter paper. In other cases where a higher temperature would be injurious the substance may be placed under a bell-jar which also incloses a dish containing sulphuric acid. The operation proceeds more quickly if the bell-jar is connected with an air-pump and thus rendered vacuous.

Substances which do not decompose at 100° are best dried in a copper oven provided with a jacket containing water which is heated to boiling, the water-level being kept constant by means of an overflow *a* and feeding arrangement

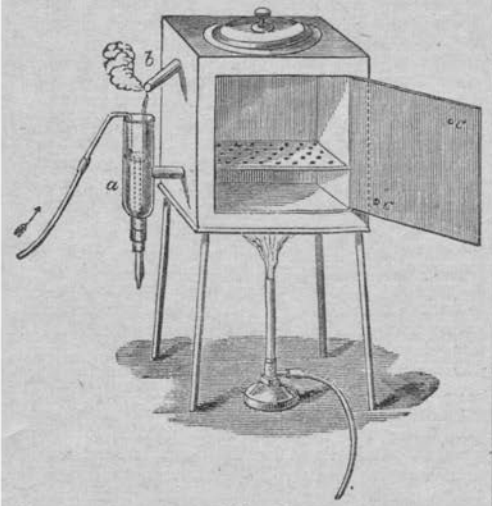


FIG. 2.

at the side. The inside of the oven is fitted with a perforated shelf which supports dishes, funnels, &c. (Fig. 2).

When the substance is sufficiently stable it is advisable to dry at 115°–120°, since an increase of 10° or 20° often greatly reduces the time required. For this purpose we use a copper oven without a jacket, heated by a lamp underneath; or toluene, boiling at 110°, may be used instead of water in the oven with a jacket; crude xylene will give a higher temperature (129°). Inside the oven at a little distance from the bottom is a shelf which supports the vessel containing the substance. At the top of the oven are two apertures, one of which serves to promote a current of air through the oven, whilst the other carries a thermometer the bulb of which is close beside the vessel which is being heated.

If it is desired to keep the temperature constant for a long time, the oven must be provided with a thermoregulator (*v.* THERMOREGULATORS).

Weighing.—The balance and the precautions to be observed in weighing form the subject of a special article (*v.* BALANCE). As a rule, substances taken for analysis should be weighed from tubes provided with well-fitting stoppers or corks, or from weighing bottles fitted with glass capsule stoppers, the difference between the weight of the tube or bottle before and after the removal of the substance giving the weight taken for analysis. The quantity required for an analysis will depend upon circumstances. When constituents present in minute quantity have to be estimated, a relatively large amount of the substance is required, but for the estimation of one or two constituents from 1 to 2 grams of the substance is usually sufficient. The smaller the quantity of matter operated upon, the shorter the time required for filtration, washing, &c., but also the greater the demands on the skill and accuracy of the operator.

Hygroscopic substances and precipitates must be kept under a *desiccator* (*q.v.*), *i.e.* a glass dish containing sulphuric acid or calcium chloride, fitted with a tray to support a crucible, &c., and provided with an air-tight glass cover, preferably bell-shaped. Crucibles containing non-hygroscopic precipitates may be allowed to cool with exposure to air, provided that the empty crucibles were allowed to cool under the same conditions before weighing.

Solution.—The solution of a substance is most conveniently effected in flasks or in somewhat deep beakers which are inclined at an angle in order to prevent possible loss by spurting. The operation may be accelerated by heat, and the reagent should be used in the most concentrated form possible and in the least possible excess, in order to avoid loss of time in evaporation, &c. Evaporation to expel excess of solvent should, where possible, be conducted in the same vessel.

Evaporation.—The evaporation of a liquid may be effected over an ordinary bunsen flame, or over a rose burner, care being taken that the liquid does not boil. If the operation is conducted in a flask or crucible, the latter should be inclined in order to prevent loss by ebullition, and the operation is accelerated in the first case by drawing a current of air through the flask, in the second by inclining the lid of the crucible (Fig. 3) across the mouth of the vessel and thus producing a circulation. The rate of evaporation, *cæteris paribus*, depends on the area of surface exposed, and hence the operation is effected most quickly in shallow dishes, especially if a current of air removes the vapour as fast as it is given off. During the process the contents of the dish should be protected from dust, &c., and this is really done by supporting at a distance of about six inches above the surface of the dish a triangle of glass rod or tubing on which is stretched a sheet of filter paper freed from soluble compounds by treatment with acid. When evaporation over a direct flame is impracticable, the dishes, &c., should be placed on a *water-bath*, that is, a vessel containing boiling water, in such a way

that they are heated by the steam. The top of the water drying-oven already described (Fig. 2) may be provided with a series of rings of various

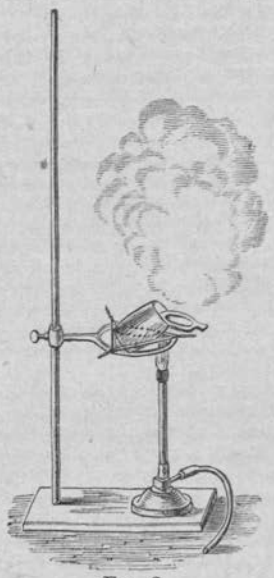


FIG. 3.

sizes and thus serves two purposes. Ordinary tin cans or copper vessels of similar shape will answer, but in all cases it is desirable to have an arrangement for keeping the water at a constant level.

Precipitation is conducted in beakers, dishes, or conical flasks, but not in ordinary round flasks because of the difficulty of removing the precipitate. Glass vessels, especially when new, are appreciably attacked and dissolved by water, and still more strongly by alkaline solutions, the action increasing with the concentration of the solution and the duration of contact. For quantitative work Jena glass vessels should be used, as these are least affected by alkalis. Acid liquids, with the exception of dilute sulphuric acid, have less solvent action. Porcelain vessels, especially after they have been used for a short time, are not appreciably attacked (Fresenius's Quant. Anal.). All precipitations involving long heating with alkaline liquids should be conducted in porcelain vessels or in platinum, silver, or nickel dishes. Silica-ware vessels can be used with all acid liquids excepting those evolving hydrogen fluoride (Zeitsch. anorg. Chem. 1905, 44, 221).

Unless circumstances forbid, the liquid and the reagent should be heated to boiling and mixed gradually with continual agitation, since under these conditions precipitation as a rule is more rapid and complete, and the precipitate is obtained in a dense and granular form and is readily separated and washed. Usually filtration may be commenced as soon as the supernatant liquid is clear, or at any rate after two or three hours. An unnecessary excess of reagent should always be avoided, but in all cases complete precipitation should be proved by adding a small quantity of the reagent to the clear liquid.

Filtration.—The separation of a precipitate from a liquid is usually effected by means of a specially prepared variety of blotting paper, known as filter paper. The Swedish paper made by J. Munktell has the oldest reputation, but that made by Schleicher and Schull, of Düren, is of excellent quality, and for many purposes answers better. The latter firm supply paper which has been treated with hydrochloric and hydrofluoric acids, and thus freed from almost all inorganic matter. Filter papers of similar quality are also supplied by Max Dreverhoff, and by Baker and Adamson. It is desirable that all paper used in quantitative work should be free from soluble compounds, and this end is secured by soaking the ordinary filter paper for three or four hours in pure hydrochloric acid diluted with 15–20 times its volume of water, and then washing thoroughly to remove all traces of acid and soluble salts. The paper is conveniently kept in circular pieces of known radii (2, 4, 5, 6, 8 cm.), and the ash left by each size should be determined once for all by incinerating six filters of one of the medium sizes in the manner described under the treatment of precipitates, and weighing the ash which is left. This quantity divided by six gives the average amount of ash left by one filter of that size, and the amount left by the other sizes is readily calculated, the quantity of ash being proportional to the area of the paper.

Usually the filter paper is supported in a glass funnel which should have smooth even sides and an angle of 60°. The stem should be somewhat long and not too wide, with the lower end cut obliquely. A circular filter is folded in half, then in a quadrant, and when the quadrant is opened at one side it forms a hollow cone which should fit accurately into the funnel. The edge of the filter paper should be about 10 mm. below the edge of the funnel, and the size of the filter should be such that it is not more than three quarters filled by the precipitate. After placing the filter in position it is moistened with water, and fitted accurately to the glass, care being taken to remove all air bubbles from between the glass and the paper. Attention to these points greatly facilitates the subsequent filtration. The edge of the vessel containing the liquid to be filtered is slightly greased outside, and the liquid is directed into the filter by means of a glass rod, care being taken not to disturb the precipitate until most of the clear liquid has passed through. It is advisable to keep the filter well filled with the liquid, but the latter must not rise higher than 10 mm. below the top of the paper.

In order to accelerate filtration a glass tube about 3–4 mm. in diameter and not less than 20 cm. long, bent into a loop near its upper end, may be attached to the stem of the funnel by means of indiarubber tube.

Greater rapidity of filtration is obtained by using one of the numerous water pumps (*v.* FILTER PUMP). In this case the liquid is filtered into a flask with stout walls, preferably of the conical form. The stem of the funnel passes through a cork which fits in the neck of the flask and also carries a tube connected with the pump, or the flask may be provided with a side tube for this latter purpose. When it is required to filter into a dish or beaker, the latter is placed

under a tubulated bell-jar standing on a glass plate, the cork carrying the funnel, &c., being fitted into the tubulus of the bell-jar. If the reduction of pressure is considerable, it becomes necessary to support the apex of the filter. In the case of filters of medium size the necessary toughness is obtained by dropping into the apex of the dry filter, after it has been fitted into the funnel, two or three drops of the strongest nitric acid. After a minute or two the paper is washed and is ready for use. Bunsen's original method is to support the apex of the filter by means of a cone of platinum foil, which is made in the following way. A circular piece of thin platinum foil 3–4 cm. in diameter is cut in the manner shown in the diagram (Fig. 4), softened by heating in a flame, and then placed against a small metal cone of 60°, so that the point *a* coincides with the apex of the cone. The foil is then folded round the metal so that it also forms a small cone, which is finished by being pressed in a hollow conical mould into which the metal cone fits. It is then dropped into the funnel and the paper fitted in. The metal cones and moulds required can be purchased; Bunsen's method of making a cone and mould of plaster is described in Thorpe's Quantitative Analysis.

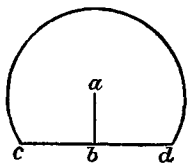


FIG. 4.

Carmichael has described a method of reverse filtration (Zeitsch. anal. Chem. 10, 83).

The Gooch crucible (Chem. News, 37, 181), which has a perforated bottom lined with a thin asbestos mat, has now become a recognised means of collecting precipitates. The asbestos makes an excellent filter, is not affected by ordinary acid and alkaline liquids, is readily dried, and does not alter in weight when ignited. The quality of the asbestos is of prime importance, a non-ferruginous amphibole being preferable to the cheaper hydrated varieties of serpentine which are appreciably soluble in acids. Silky asbestos is scraped into a short fine down, boiled with hydrochloric acid, well washed, and kept in water. A platinum or silica crucible, preferably of the low wide form, with the bottom perforated with a large number of minute holes, is fitted air-tight into an ordinary funnel by means of an indiarubber ring placed between the crucible and the wall of the funnel, which is fitted into a filtering flask. The pump is set in action and water containing the asbestos in suspension is poured into the crucible. A layer of asbestos felt is quickly formed, and when this is of sufficient thickness it is drained, dried, and ignited over a lamp, and the crucible is then weighed. It is desirable to have a non-perforated bottom to fit on the crucible during ignition, in order to protect the contents of the crucible from the flame gases. A Soxhlet tube, having a perforated porcelain or platinum disc covered with an asbestos layer and supported at the constricted part of the tube, is frequently used to collect precipitates. Neubauer recommends a perforated platinum crucible with a felted platinum mat (Zeitsch. anorg. Chem. 1901, 922; *cf.* Amer. Chem. J. 1909, 31, 456). The weighed crucible is replaced in the funnel, and filtration is conducted in the ordinary way, care being taken that the pump is set in action before any liquid is poured into the crucible. Drying and igniting the precipitate occupies but little time. For gelatinous precipitates the crucible may be replaced by a cone, the lower part of which is made of platinum gauze and the upper part of platinum foil.

Gooch has proposed (P. Am. A. 1885, 390; Zeitsch. anal. Chem. 24, 583) in special cases to replace the asbestos by anthracene, which after filtration can be dissolved in benzene or other suitable solvent, leaving the precipitate undissolved.

Not unfrequently it is necessary to keep the contents of a funnel hot during filtration. This is effected by placing the funnel inside a copper jacket filled with water which is heated to boiling by means of a side tube. A simpler plan is to coil lead pipe round the funnel and blow steam through the pipe (Richter, J. pr. Chem. (ii.) 28, 309).

Sometimes it is desirable to avoid contact with air during filtration. A convenient apparatus for this purpose has been described by Klobukow (Zeitsch. anal. Chem. 24, 395; J. Soc. Chem. Ind. 4, 756).

All precipitates require to be washed in order to remove soluble impurities, the liquid employed being water, dilute acid, dilute ammonia, alcohol, &c., as the case may require. The object in all cases is to reduce the impurity to the desired minimum in the shortest possible time with the least expenditure of liquid, and it can readily be shown that successive treatments with small quantities of the liquid are far more effectual than the same volume of liquid applied all at once (Bunsen, Annalen, 148, 269). Whenever possible hot liquids should be used, and the precipitate should be washed so far as possible by decantation, only the washing liquid being poured on the filter. The soluble impurity collects round the top edge of the filter paper by reason of capillary action and evaporation, and hence, when washing is effected with the aid of an ordinary wash-bottle with a movable jet, it is important that the liquid should be directed on to the top edge of the filter. It is also important that each quantity of wash-water should be drained away as completely as possible before adding a fresh quantity, and it is obvious that this takes place most readily when a pump is used. In this case the liquid is poured into the funnel from an open vessel to a height of about 10 mm. above the edges of the paper. Care must be taken that the precipitate is not drained so far that channels are formed. It is always advisable to ascertain whether the washing is complete by testing a few drops of the last wash-water.

Drying and weighing precipitates.—Occasionally a precipitate must be dried without the application of heat, and this is accomplished in a desiccator over sulphuric acid, preferably in a vacuum. In other instances the substance is not injured by a temperature of say 120°, but cannot be ignited. In these cases the filter is carefully dried at the particular temperature, enclosed between a pair of watch-glasses, and weighed. It is then placed in the funnel and the operation proceeded with. After filtration the filter and the precipitate are thoroughly dried at the same temperature as before and

again weighed, the increase being the weight of the precipitate. Tared filters can, however, be generally replaced by Gooch crucibles, Soxhlet tubes, &c. The majority of the precipitates usually met with can, moreover, be dried by heating them in a crucible over a lamp. In most cases it is not necessary that the precipitates should previously be dried. The greater part of the water is removed by draining in the funnel by means of the pump or by placing the filter and its contents on a porous tile or on a pad of filter paper. The filter is then introduced into a crucible, heated cautiously until quite dry and then heated more strongly until the weight is constant.

When the precipitate is not easily reducible it is not necessary to remove the paper before ignition. The wet paper enclosing the precipitate is placed in a platinum crucible, and the latter heated with a full flame; the water present assumes the spheroidal state and the paper smoulders away without spurting. If any slight reduction takes place, for example, with barium sulphate, it is easily remedied by adding a few drops of dilute sulphuric acid and again heating. In the case of magnesium pyrophosphate strong nitric acid serves a similar purpose. If, however, the precipitate is readily reduced in contact with organic matter, it must be removed from the paper as completely as possible by gentle friction, and transferred to the crucible, which should stand on a sheet of glazed paper. A carefully trimmed feather or a camel's-hair brush is useful to transfer scattered particles from the paper to the crucible. The filter paper is then folded with the portion to which the precipitate had adhered inside, wrapped in platinum wire which forms a sort of cage, and set on fire. Whilst burning it is held over the crucible, and *when completely burnt out*, the ash is heated with the tip of a Bunsen flame for a few minutes and then shaken into the crucible.

Precipitates which contain compounds of silver, lead, zinc, tin, and other easily reducible metals, should be heated in porcelain crucibles, since platinum vessels are liable to be attacked. Care should also be taken that platinum vessels are not heated with smoky or 'roaring' flames, and do not come in contact with brass crucible tongs or easily fusible metals whilst hot. After some time the surface of the metal may become dull, owing to the partial disaggregation of the platinum, but this defect can be remedied by polishing the metal with sea-sand or a burnisher.

Heating appliances.—The ordinary bunsen burner serves for most operations, but the argand bunsens introduced by Fletcher are more efficient, and the radial slit burner of the same inventor is perhaps the most efficient gas-burner for heating purposes that has yet been made. Glass vessels are more safely heated on a sheet of wire gauze or on a layer of sand in a metal tray. A most useful piece of apparatus in a technical laboratory is a large iron plate supported on iron legs, and heated by a burner underneath the middle. Vessels placed on the plate near its edges are subjected to a very gentle heat, but may be raised to a much higher temperature by being moved nearer to the middle.

A water-bath provided with a constant feeding arrangement is the most useful way of heating vessels at 100°. If higher temperatures are needed, a saturated solution of calcium chloride, melted paraffin, or oil may be used. Maumené (Compt. rend. 1883, 97, 45, and 215) has proposed to use fused mixtures of alkaline nitrates for temperatures between 140° and 250°. Brauner (Chem. Soc. Trans. 1885, 47, 887) has described a simple arrangement for heating substances in sulphur vapour.

Reagents.—The ordinary acids and ammonia are required in a dilute as well as in a concentrated form. Whenever possible the reagents should be made in solutions the strengths of which are multiples or submultiples of normal solutions. A convenient strength for the dilute mineral acids is twice normal, and the alkaline solutions should be of equivalent strength.

Qualitative Analysis.

The detection of the constituents of a mixture or chemical substance is based on the fact that almost every metallic or acidic radicle will under suitable conditions give rise to a reaction which, under these conditions, is characteristic and thus enables one to distinguish this radicle from all others. These tests may be applied directly to the solid substance, usually at high temperatures, when they are known as *dry reactions;* or they may be employed in solution, in which case they are described as *wet reactions*. The wet and dry reactions of metallic and acidic radicles are generally, but by no means invariably, independent of the acidic and metallic radicles with which they are respectively combined.

Examination in the Dry Way.

The indications obtained from the dry reactions of a substance frequently afford very suggestive clues to its composition, but as these tests rarely, if ever, indicate the relative proportions in which the constituents exist in the mixture under examination, they must be regarded as being preliminary to the more systematic examination of the substance in solution. Moreover, negative results obtained from dry tests must not be accepted as final evidence.

In all cases, however, a preliminary examination of the substance should be made in the dry way, and if the substance is in solution a portion should be evaporated to dryness. The reactions of several substances in the dry way are interfered with and rendered inconclusive by the presence of certain other substances; but nevertheless an examination of this kind often gives much information in a short time.

The most convenient source of heat for this purpose is the ordinary bunsen burner. This consists of a metal tube at the base of which coal gas enters by means of a jet, the lower part of the tube being pierced with holes through which air is drawn and mixed with the coal gas. The mixture of 1 volume of coal gas with about 2½ volumes of air, which is thus produced, burns at the top of the tube with a non-luminous flame. When the supply of gas is turned low, it is necessary also to reduce the air supply by partially closing the inlet holes by means of a regulator. The upper part of the burner is generally fitted with a support carrying a cone to protect the flame from draughts.

The flame consists essentially of an inner

dark zone containing unburnt gas mixed with air, and an outer zone or flame mantle in which combustion becomes complete. If the air holes are partially closed, a luminous cone appears at the top of the inner zone. Bunsen has shown, however, that several distinct zones exist, each of which can be utilised for producing particular reactions. The most useful of these are *a*, a comparatively cold zone at the base of the flame, which serves for the volatilisation of salts in order to obtain flame colourations; the *lower reducing flame* δ about one quarter of the way up and close to the edge of the dark zone; η, the *upper* and more powerful *reducing flame* at the top of the dark zone, obtained by closing the air holes until the tip of the inner zone just becomes luminous; β, the *zone of fusion* or highest temperature, at about one-third the height of the flame and half-way between the inner zone and the flame mantle; γ, the *lower* and hotter *oxidising flame* at the edge just below the zone of fusion; and ε, the *upper oxidising flame* at the extreme tip of the flame.

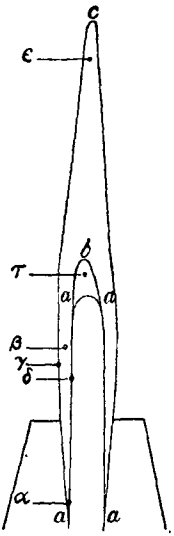


FIG. 5.

Instead of the bunsen burner, the flame obtained by means of a blowpipe may be used; a mouth blowpipe consists of a metal tube provided at one end with a mouthpiece, the other end fitting into a small metal box which serves to condense and retain the moisture of the breath. From the side of this box a second shorter and narrower tube projects at right angles to the first, and is provided with a nozzle or jet of brass or, better, of platinum. For general work the diameter of the bore of the jet should be

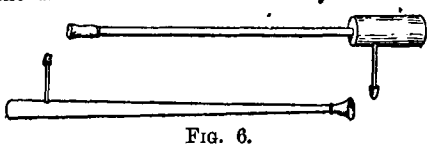


FIG. 6.

0·4 mm. In Black's blowpipe the larger tube is conical, the lower and wider end serving the same purpose as the box in the form just described. The art of keeping up a continuous blast of air through the blowpipe can only be acquired by practice. The necessary pressure is produced by distending the cheeks, breathing being carried on through the nostrils, whilst communication between the nostrils and the mouth is cut off by the pressure of the tongue against the palate. A convenient form of hand-blower for blowpipe work has been devised by Fletcher.

A good flame for blowpipe work is obtained by dropping into the tube of an ordinary bunsen burner a brass tube, the lower end of which descends to the bottom of the burner and cuts off the supply of air, whilst the upper end is flattened and cut off obliquely. The flame should be much smaller than when the burner is used in the ordinary way. Coal gas usually contains more or less sulphur, and consequently cannot be used when testing for this element.

A thick stearin candle answers well; but nothing is better than a lamp consisting of a low and rather wide cylindrical metal vessel, open at the top, with a somewhat broad and flat wick-holder attached to the side. The fuel used is solid paraffin, which is kept in a melted condition by the heat of the blowpipe flame, the wick being so arranged that the flame passes over the top of the paraffin. A metal cover protects the lamp from dust when not in use.

The nozzle of the blowpipe is introduced a short distance into the lamp flame at a short distance above the wick, and when the blast is produced the flame is deflected horizontally, becomes long and narrow, and is seen to consist of two parts, viz. an *outer* or *oxidising* flame, at the tip of which there is an excess of oxygen

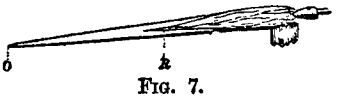


FIG. 7.

heated to a high temperature, and an *inner* or *reducing* flame, which contains carbonic oxide and hydrocarbons heated to a high temperature. If the blowpipe is held just at the edge of the flame and a moderate blast is used, a broader reducing flame can be obtained, which has a luminous tip containing solid particles of carbon.

The following appliances are required: a small pair of forceps with platinum points; short pieces of thin platinum wire; charcoal from some fine-grained compact wood; glass tubes about 3 mm. internal diameter, and 60–80 mm. long, closed at one end; and glass tubes of similar diameter 100–120 mm. long, open at both ends and bent slightly in the middle. The reagents used are borax, microcosmic salt (NH_4NaHPO_4, $4H_2O$), potassium cyanide, sodium carbonate, potassium nitrate, cobalt nitrate solution, and potassium hydrogen sulphate.

The dry tests are conveniently performed in the following order:—

(1) *Heating in a dry closed tube.*—To avoid soiling the sides of the tube, the substance should be introduced by means of a roll of stiff paper. The following changes may be observed:

(*a*) Carbonisation with or without evolution of empyreumatic vapours = *organic compounds.*

(*b*) Condensation of moisture on cold parts of tube; neutral reaction = *hydrated salts and hydroxides*; acid reaction = *acids and acid salts*; alkaline reaction = *ammonium salts.*

(*c*) Fusion without change of colour = *alkaline salts, hydrated salts.*

(*d*) Fusion with change of colour = yellow hot, dark yellow cold = *bismuth oxide*; yellow hot, red cold = *lead oxide.* The chromates of lead and the alkali metals fuse and darken on heating.

(*e*) No fusion, but change of colour: dark yellow hot, pale yellow cold = *stannic oxide*; yellow hot, white cold = *zinc oxide*; black hot, reddish-brown cold = *ferric oxide*; black hot, bright red cold = *mercuric oxide*; brown darkening on heating = *cadmium oxide.*

(*f*) Gas evolved: oxygen = *oxides, peroxides, chlorates, bromates, perchlorates, iodates, periodates, persulphates,* and *nitrates*; carbon djoxide = *carbonates, bicarbonates, oxalates*; carbon monoxide (blue flame) = *formates, oxalates*; sulphur dioxide = *acid sulphites, sulphates of heavy metals* (together with sulphur trioxide); cyanogen = *cyanides of heavy metals*; ammonia = *ammonium salts*; phosphine = *phosphites, hypophosphites*; orange-brown vapours = *nitrates, nitrites, bromides*; violet vapours = *iodides*; colourless fuming gas = *hydrated chlorides.*

(*g*) Sublimate: white infusible = *arsenious oxide* (octahedra), *antimonious oxide* (needles), *selenium dioxide, ammonium chloride, ammonium sulphite* (from ammonium sulphate); white fusible = *mercuric chloride, tellurium dioxide, organic acids, molybdenum trioxide* (at very high temperatures); coloured, black, or reddish black = *selenium, mercuric sulphide*; yellow hot, red cold = *mercuric iodide*; reddish yellow = *arsenious sulphide*; yellow = *sulphur* and *sulphides*; black metallic mirror = *arsenic*; grey metallic globules = *mercury.* These metallic sublimates are often obtained nore readily by heating the material with potassium cyanide.

Phosphorus compounds are detected by heating in a closed tube with magnesium ribbon and dropping the hot tube into water, when inflammable phosphine is evolved.

(2) *Heating in open tube.*—The tube being inclined, to promote a current of air through it, the changes observed are similar to the reactions in the closed tube, but sulphides burn evolving sulphur dioxide; arsenic is oxidised to arsenious oxide, and selenium and its compounds evolve a pungent odour of horseradish (dioxide), and give a grey or reddish sublimate.

(3) *Heating on platinum wire.—Flame colourations.*—The wire being cleaned by repeated dipping in hydrochloric acid and heating till it imparts no colour to the flame, a small quantity of the substance supported on the end of the wire is introduced into zone *a* of the bunsen flame. As a colouration is produced only if volatile compounds of the metals are present, the substance should be moistened with hydrochloric acid to produce the volatile chlorides. This result may also be attained by mixing the substance on an asbestos thread with moist silver chloride, a compound which, while imparting no colour to the flame, slowly yields chlorine, converting other metals into chlorides. The wire should be slowly moved into the hottest part of the blowpipe or bunsen flame, so that the colourations due to less volatile constituents may be successively developed.

Colourations: yellow = *sodium*; orange red = *calcium*; crimson = *strontium*, *lithium*; lavender = *potassium, rubidium, cæsium*; apple green = *barium*; bright green = *thallium, copper, boric acid*; pale blue = *lead, antimony*; deep blue becoming green = *copper halides*; deep blue = *selenium.*

The pocket spectroscope (direct vision) is a useful aid in examining flame colourations, particularly in the case of strontium and calcium, which exhibit respectively a characteristic blue and a yellowish-green line.

(4) *Heating on charcoal.*—The substance mixed with three times its weight of dry sodium carbonate or of a mixture of 2 parts sodium carbonate and 1 part potassium cyanide, is placed in a small shallow hole scooped out in charcoal, and heated in a reducing flame. The metallic bead obtained is examined as to colour, malleability, solubility, &c. Many metals yield films of oxide, which coat the charcoal at a greater or less distance from the flame, and the colour and appearance of which are more or less characteristic. These and similar films are best seen when the charcoal is supported on an aluminium plate (Ross). A piece of sheet aluminium 12 cm. by 5 cm. is bent in right angles at a distance of 2 cm. from one end, thus forming a ledge on which a small flat piece of charcoal is placed, the plate being held so that the surface rises vertically behind the ledge. Volatile oxides, &c., condense on the metallic surface (*v.* Hutchings, Chem. News, 1877, 36, 208, 217).

The reduction may also be effected by adding a fragment of sodium to the substance supported on charcoal (Parsons, J. Amer. Chem. Soc. 1901, 23, 159).

In order to obtain reduced metals with the bunsen flame, a match-stick is smeared with ordinary sodium carbonate (washing soda) which has been melted by holding it in the flame, and the wood thus prepared is carbonised by heating it in the flame. A small quantity of the substance is mixed in the palm of the hand with a small quantity of the fused washing soda, and the mixture is carefully placed on the charcoal splint, which is then heated in the lower or upper reducing flame. When reduction is complete, the match is allowed to cool inside the dark zone, and is then withdrawn, crushed in a mortar, and the lighter particles of charcoal removed by levigation with water, the heavy metallic particles being left.

By means of the bunsen flame reduced metals and their oxides can be obtained in the form of films on a porcelain surface. The substance is supported on a long slender piece of asbestos, and heated in the tip of a small oxidising or reducing flame, a small evaporating dish containing cold water being held momentarily just above the asbestos (*v.* Bunsen's Flammenreactionen, Heidelberg, 1880).

Incrustations on charcoal: white, very volatile = *arsenic*; white, less volatile = *antimony*; orange-yellow hot, pale yellow cold = *bismuth*; pale yellow hot, deep yellow cold, white edge = *lead*; yellow hot, white cold = *zinc, molybdenum*; reddish-brown or orange-yellow cold = *cadmium.*

Metallic beads or residues on charcoal: white malleable = *silver, tin, lead*; red malleable = *copper*; grey brittle = *antimony, bismuth*; grey powder, magnetic = *iron, cobalt, nickel*; non-magnetic = *molybdenum.*

(5) *Cobalt nitrate reactions.*—Certain *infusible* substances, when moistened with cobalt nitrate solution and strongly heated, acquire characteristic colours. These reactions are frequently, but not necessarily, carried out on a charcoal support:—blue infusible mass = *aluminium*; blue fusible = *certain phosphates, silicates, borates*; green = *zinc, titanium, tin*; pink = *magnesium.*

(6) *Heating with borax or microcosmic salt.*—A small loop is made at the end of a platinum wire, to which some borax or microcosmic salt is

made to adhere, and heated in the flame until fused. The bead when cold must be quite transparent and colourless, otherwise it must be remelted, shaken off, and a fresh bead made. A *small* quantity of the substance is taken on the bead and heated first in the oxidising flame (O.F.) and then, after it has been examined, in the inner or reducing flame (I.F.). The colour of the bead should be observed both hot and cold. If too much substance is taken, the bead becomes opaque, and the colour cannot be distinguished.

These so-called borax and microcosmic beads owe their colour respectively to the formation of certain borates and phosphates of the heavy metals. Borax glass consists of anhydrous $Na_2B_4O_7$, and when heated with a metallic oxide or salt the excess of boric oxide present unites with the metallic oxide, forming the corresponding borate:

$$Na_2B_4O_7 + CoO = Na_2B_2O_4 + CoB_2O_4 \text{ (blue)}.$$

Microcosmic salt on ignition yields the readily fusible sodium metaphosphate, and this salt combines with metallic oxides to form double orthophosphates:

$$NaPO_3 + CuO = CuNaPO_4 \text{ (green)}.$$

When a silicate is introduced into the molten metaphosphate, the latter withdraws the basic oxide from the former, setting free silica, which remains undissolved ('silica skeleton'):

$$CaSiO_3 + NaPO_3 = CaNaPO_4 + SiO_2.$$

Borax beads.—

Inner flame		Outer flame		Metal
Hot	Cold	Hot	Cold	
Green	Bottle-green	Yellow	Paler	*Iron*
Green	Green	Yellow	Green	*Chromium*
Green	Bottle-green	Yellow	Pale yellow	*Uranium*
Colourless	Colourless	Amethyst	Amethyst	*Manganese*
Blue	Blue	Blue	Blue	*Cobalt*
Grey	Grey	Violet	Reddish-brown	*Nickel*
Brownish	Emerald-green	Yellow	Greenish-yellow	*Vanadium*
Colourless	Brown	Green	Bluish-green	*Copper*
Colourless	Colourless	Orange-red	Colourless	*Cerium*
Brown	Brown	Yellow	Colourless	*Molybdenum*
Brownish-violet		Yellow	Colourless	*Titanium*
Yellow to brown		Yellow	Colourless	*Tungsten*

Microcosmic beads.—The colours produced are similar to those in the borax bead, but the reducing effects are less pronounced. In the I.F. molybdenum compounds give a green colour, and those of tungsten a greenish-blue tint. Chlorides and bromides evolve a blue and green flame when heated with a microcosmic bead saturated with copper oxide, and iodides give a green flame.

(7) *Other special dry tests.*—(*a*) Heating on charcoal with potassium (or cuprous) iodide and sulphur: crimson incrustation = *bismuth*; lemon yellow incrustation = *lead*; greenish-blue fumes = *mercury*.

(*b*) Heating on charcoal with (i.) fusion mixture (Na_2CO_3,K_2CO_3) alone and moistening with dilute acid, hydrogen sulphide evolved = *sulphur compounds*; (ii.) fusion mixture and sulphur, soluble mass giving coloured precipitate with dilute acid, yellow = *tin*; orange = *antimony*. The fused insoluble oxides SnO_2 and Sb_2O_4 can be thus characterised.

(*c*) Heating with fusion mixture and potassium nitrate: soluble green mass = *manganese*; yellow mass = *chromium*.

(*d*) Heating in closed tube with potassium hydrogen sulphate. Gas evolved: carbon dioxide = *carbonates, oxalates*; accompanied by charring of the residue = *tartrates, citrates*, &c.; carbon monoxide (blue flame) = *formates, oxalates*; sulphur dioxide = *sulphites, thiosulphates*; hydrogen sulphide = *sulphides* (not all); hydrogen chloride (fuming in air) = *chlorides* (not all); hydrogen fluoride (etching glass) = *fluorides*; bromine and hydrogen bromide = *bromides*; iodine = *iodides*; nitrous fumes = *nitrites, nitrates*.

Examination in the Wet Way.

The preparation of the solution requires some attention. A metallic substance is treated at once with moderately strong nitric acid. Tin and antimony form oxides which to a great extent remain undissolved; arsenic is oxidised to soluble arsenic acid; other metals (with the exception of gold and the platinum metals, which are not attacked) are converted into nitrates, which dissolve at once or on diluting.

If the substance is not a metal, it is first treated with hot water, and if anything is dissolved (which is ascertained by evaporating a few drops on platinum foil), the substance is boiled two or three times with fresh quantities of water. Any residue which may be left is treated with dilute hydrochloric acid, and afterwards, if necessary, with the concentrated acid. Care must be taken to observe if any gas is given off—*e.g.* carbon dioxide (effervescence), from *carbonates*; sulphur dioxide, from *sulphites* or *thiosulphates*; chlorine, from *peroxides* or *hypochlorites*; hydrocyanic acid, from *cyanides*; hydrogen sulphide, from *sulphides*. Many chlorides are insoluble in the strong acid, and hence the solution must be diluted before filtering. Silver, lead, and univalent mercury will be converted into insoluble chlorides.

Solvent action of the mineral acids (*v.* A. A. Noyes and W. C. Bray, J. Amer. Chem. Soc. 1907, 29, 137, 481).—In dealing with substances insoluble in water the following acidic solvents may be used: hydrochloric, nitric, sulphuric, and hydrofluoric acids. Although it is impossible to give a hard-and-fast rule as to the way in which these agents should be applied, the following considerations will indicate the relative advantages of one or other of these solvents:—

Hydrochloric acid.—(1) Advantages: (i.) Solutions on this acid do not yield a precipitate of sulphur on treatment with hydrogen sulphide; (ii.) the solvent action of this acid on the following oxides: lead peroxide, manganese dioxide, and the hydrated oxides of tin and antimony, is superior to that of nitric acid; (iii.) hydrated silica is readily precipitated on evaporating the hydrochloric acid solution.

(2) Disadvantages: (i.) This acid is comparatively useless for alloys; (ii.) evaporation of the hydrochloric acid solution leads to the volatilisation of arsenic, mercury, tin and selenium as chlorides.

Nitric acid.—(1) Advantages: (i.) The best general solvent for the metals and their alloys; (ii.) oxidises and dissolves insoluble compounds of arsenic, mercury, and selenium without the formation of volatile compounds of these

elements; (iii.) does not cause the precipitation of silver or lead; (iv.) oxidises sulphides not attacked by hydrochloric and sulphuric acids.

(2) Disadvantages: (i.) This acid alters the state of combination of many elements, *e.g.* it oxidises mercurous, arsenious, antimonious, stannous, and ferrous salts; (ii.) its solution deposits much sulphur on treatment with hydrogen sulphide; (iii.) the oxidation of sulphides by nitric acid in the presence of barium, strontium, and lead leads to the precipitation of these metals as sulphates; (iv.) nitric acid is less efficacious than hydrochloric acid in rendering hydrated silica insoluble.

The nitric acid solution of an alloy when evaporated to dryness and heated at 120°–130° may yield the partially dehydrated hydroxides of silica, tin, antimony, titanium, and tungsten in an insoluble condition. When phosphorus or arsenic is present together with tin the so-called stannic phosphate or arsenate (phosphostannic or arsenostannic acid) may also be found in the insoluble residue.

Sulphuric acid.—The dilute acid is of little value as a solvent, but the hot concentrated acid has been found useful in certain cases. (i.) In bringing certain alloys into solution, *e.g.* white metals (*v.* Low, J. Amer. Chem. Soc. 1907, 29, 66); (ii.) destruction of organic matter; evaporation of a concentrated sulphuric acid solution of the substance is preferable to ignition, because the latter process renders certain compounds insoluble and leads to the loss by volatilisation of such elements as mercury, arsenic, selenium, &c. Very stable organic substances (*e.g.* paraffin and cellulose) can be destroyed completely by adding a little strong nitric acid and heating till the solution acquires a light yellow colour. When diluted considerably with water (20–30 vols.) this solution may yield a deposit containing silica and certain refractory silicates and fluosilicates, together with the sulphates of barium, strontium, lead, calcium, and chromium (an insoluble sulphate formed during the heating), basic sulphates of bismuth, antimony, and tin and the ignited oxides of the last two metals with those of aluminium and titanium. (iii.) Insoluble compound cyanides are decomposed by hot concentrated sulphuric acid, but may also be attacked by aqueous alkali hydroxides yielding soluble alkali cyanides and insoluble metallic hydroxides.

Hydrofluoric acid.—The insoluble residues from the preceding acids may be treated with a 40 p.c. solution of hydrogen fluoride, which is now obtainable in glass bottles lined with paraffin wax. (1) Advantages: (i.) Many insoluble silicates are readily decomposed, the silicon being eliminated completely as gaseous silicon fluoride; (ii.) the reducible metals and their compounds may be treated in platinum basins or crucibles providing that the solution is never evaporated to dryness.

(2) Disadvantages: (i.) Glass or silica-ware vessels cannot be used with hydrofluoric acid; (ii.) owing to the destructive action of hydrogen fluoride on animal tissues, all operations with solutions of this gas must be conducted in an efficient draught cupboard.

Aqua regia (concentrated hydrochloric acid 3 parts and nitric acid 1 part) may be employed in attacking substances not dissolved by hydrochloric or nitric acid, although it is of little use for colourless insolubles. It readily dissolves gold and platinum, but is less efficacious in rendering soluble the rarer noble metals (*e.g.* osmium and iridium).

Treatment of Insolubles.

The substances not dissolved by the foregoing acidic reagents are generally regarded as insolubles, although they are divisible into two classes: (i.) *pseudo-insolubles*, which are dissolved by certain specific solvents; (ii.) *true insolubles*, which are only broken up into soluble compounds by the agency of fused alkali carbonates.

Pseudo-insolubles.—*Silver chloride* and *bromide*, soluble in aqueous ammonia. (The three silver halides may be completely decomposed by treatment with zinc and dilute sulphuric acid, metallic silver and soluble zinc halide being produced.) *Insoluble fluorides* (those of the common and rare earth metals) are decomposed by heating with concentrated sulphuric acid. *Lead sulphate*, soluble in ammonium acetate solution; *oxides of antimony*, dissolved in hydrochloric and tartaric acids. *Anhydrous chromic sulphate* and *basic bismuth sulphate*, converted respectively into hydroxide and basic carbonate by boiling with aqueous sodium carbonate; these products are then dissolved in dilute mineral acids.

True insolubles.—These substances are fused with a mixture of sodium and potassium carbonates in equimolecular proportions (so-called fusion mixture). In the absence of reducible metals (*e.g.* silver or lead), insoluble sulphates (barium and strontium sulphates) and silicates may be heated with the fusion mixture in a platinum crucible. If any insoluble molybdenum sulphide is present (indicated by dry tests), a little nitre must be added to oxidise this sulphide, and thus prevent its corrosive action on the platinum. In the case of an insoluble silicate the fused mass is treated directly with hydrochloric acid, when the metals present pass into solution as chlorides, and the silica is rendered insoluble by evaporating down the acid solution. In the case of insoluble sulphates the fused mass is extracted with water to remove the soluble alkali sulphate, and the residue ($BaCO_3$,$SrCO_3$) is subsequently dissolved in dilute acid.

Silver iodide, bromide, and chloride are decomposed by 'fusion mixture,' yielding the soluble alkali halide; insoluble lead compounds are similarly decomposed. The strongly heated oxides of aluminium, chromium, titanium, tin, and antimony rank as insolubles; they are not readily attacked by 'fusion mixture,' but are rendered soluble by fusion with potassium hydroxide. The oxides of titanium and aluminium may be rendered soluble by fusion with potassium hydrogen sulphate; special methods for treating the insoluble oxides of chromium, tin, and antimony are indicated among the dry tests (7, *b* and *c*). The insoluble compounds of the easily reducible metals (*e.g.* Ag, Pb, Sn, Sb, &c.) can all be decomposed and reduced by fusion with sodium or potassium cyanide.

When both aqueous and acid solutions have been obtained from the same substance, the analyst must use his judgment as to whether

they may be mixed or should be analysed separately. The latter course sometimes gives information as to the distribution of the acids and bases in the original substance. If the first course is adopted, it must be borne in mind that the hydrochloric acid solution may precipitate lead and silver, and possibly mercury, from an aqueous or nitric acid solution.

Systematic Method of Examination in the Wet Way.

The formation of a precipitate at the proper stage in the systematic separation is not sufficient proof of the presence of a particular substance; some characteristic confirmatory test should always be applied. The colour of the solutions at different stages in the operation is a valuable indication. Unnecessary excess of reagents should be avoided, but filtrates should always be tested to make sure that precipitation is complete. Many tests succeed only when the proper proportion of the reagent is added, and it should be a rule always to add the reagents very gradually. All precipitates which have to be subjected to the action of reagents should be carefully washed, but in qualitative analysis it is not as a rule desirable that all the washings should mix with the filtrate.

The reaction of the original solution towards litmus paper should be noted and a portion tested for ammonium compounds by heating with sodium hydroxide or by triturating in a mortar with soda-lime (dry sodium and calcium hydroxides).

In systematic qualitative analysis advantage is taken of certain *similarities* existing between the metallic radicles which enable these radicles to be divided into a limited number of groups, the members of which are subsequently either separated or identified by means of the *differences* between the properties of their respective compounds.

The metallic radicles are divided into six groups, according to their behaviour with the following reagents, which must be applied in the order given. It may be mentioned that some chemists prefer a division into five groups, and add the reagents of Groups III. and IV. successively *without* an intervening filtration. This process is conveniently adopted in the presence of the less commonly occurring metals (J. Amer. Chem. Soc. 1908, 30, 481).

Group I.—Reagent: hydrochloric acid in moderate excess. Precipitate: *silver, lead, thallium* (*thallous*), and *mercurous chlorides*; *tungstic acid.*

If the original solution is alkaline, the group precipitate may contain sulphides (*e.g.* As_2S_3, Sb_2S_3, SnS_2) which had been dissolved in aqueous alkali sulphide or hydroxide. This yellow or orange precipitate is examined under Group II. The group precipitate may also contain insoluble silver salts (*e.g.* AgBr, AgI) precipitated from solution in alkaline cyanides or thiosulphates; these are dealt with as insolubles. The filtrate from the Group I. precipitate or the solution itself in the absence of a precipitate, must be evaporated nearly to dryness if nitric acid or nitrates are present, since these compounds lead to the precipitation of sulphur in Group II.

Group II.—Reagent: hydrogen sulphide in acid solution. Thioacetic acid has been recommended as a substitute for hydrogen sulphide in qualitative analysis (Schiff and Tarugi, Ber. 1894, 27, 2437). Precipitate: the *sulphides* of *arsenic, antimony, tin, molybdenum, gold, platinum* (*the other platinum metals*), *bismuth, lead, mercury, copper*, and *cadmium*, together with *selenium* and *tellurium*, partly free and partly as *sulphides*. The solution should be dilute and not too acid, and it should be treated and saturated repeatedly with the group reagent, since prolonged treatment is required to precipitate molybdenum and the platinum metals.

The filtrate from the foregoing sulphides is boiled to expel hydrogen sulphide, and any iron present peroxidised by warming with nitric acid or bromine water. If organic matter is present, it is destroyed either by evaporation to dryness or treatment with hot concentrated sulphuric acid (*v. supra*). Silica or barium sulphate may be precipitated at this stage. A portion of the oxidised solution should now be tested for phosphate with nitric acid and ammonium molybdate.

Group III.—Reagents: ammonium chloride and ammonium hydroxide. Precipitate: (*a*) In absence of phosphates: *hydroxides* of *aluminium, iron, chromium, glucinum, titanium, zirconium, tantalum, columbium, thorium, cerium* (*and other rare earth metals*), and *uranium* as *ammonium diuranate.* Some manganese, zinc, and alkaline earth metals may be coprecipitated. (*b*) In presence of phosphates: *the phosphates of the preceding metals, together with those of Groups IV., V., and magnesium.*

Group IV.—Reagents: ammonium sulphide or hydrogen sulphide and ammonium hydroxide. Precipitate: *sulphides* of *zinc, manganese, cobalt, and nickel.* The precipitation is carried out in the boiling solution, and the filtrate, if brown, is slightly acidified with hydrochloric acid, when *vanadium* and a small portion of the nickel are precipitated as sulphides.

Group V.—Reagents: ammonium carbonate and ammonia. Precipitate: *barium, strontium*, and *calcium* as *carbonates.*

Group VI.—The filtrate from Group V. contains *magnesium, sodium, lithium, potassium, rubidium*, and *cæsium*, which are identified by special tests.

In the absence of the rarer metallic radicles, the group precipitates are examined in the following manner. Confirmatory tests are given under special reactions.

Group I.—The precipitate is boiled with water; the aqueous extract mixed with dilute sulphuric acid gives a white precipitate ($PbSO_4$), indicating *lead.* The insoluble portion is treated with aqueous ammonia; a black residue (NH_2Hg_2Cl or NH_2HgCl and Hg) indicates *mercury*; the ammoniacal filtrate acidified with nitric acid gives white silver chloride, indicating *silver.*

Group II.—The precipitate is washed with aqueous hydrogen sulphide and warmed with yellow ammonium sulphide [$(NH_4)_2S_x$], this extraction being repeated.

(A) The filtrate is acidified with dilute hydrochloric acid, the precipitate boiled with strong aqueous ammonium carbonate, and the solution filtered; the filtrate acidified yields a yellow

precipitate (As_2S_3), denoting *arsenic*. The residue is dissolved in concentrated hydrochloric acid, the solution boiled, diluted, and treated with strips of platinum and pure zinc; a black stain on the platinum = *antimony*. The zinc is dissolved in hydrochloric acid and mercuric chloride added; a white precipitate (Hg_2Cl_2) becoming grey (Hg) = *tin*.

In the separation of arsenic, antimony, and tin by ammonium carbonate, this solvent dissolves an appreciable amount of stannic sulphide, which is reprecipitated by acids as a white oxysulphide (Schmidt, Ber. 1894, 27, 2739).

Boiling the mixed sulphides with concentrated hydrochloric acid effects a separation by dissolving the tin and antimony compounds, leaving nearly the whole of the arsenious sulphide undissolved. The mixed sulphides may also be dissolved in aqueous sodium peroxide, which produces sodium arsenate, antimonate, and stannate. On boiling this solution with excess of ammonium chloride, hydrated stannic oxide is precipitated (*v.* J. Walker, Chem. Soc. Trans. 1903, 83, 184; *cf.* Caven, Chem. Soc. Proc. 1910, 26, 176).

(B) The precipitate insoluble in ammonium sulphide is boiled with nitric acid (1 vol. acid sp.gr. 1·20 : 2 vols. H_2O), the residue dissolved in aqua regia, excess of acid expelled, and stannous chloride added; a white precipitate (Hg_2Cl_2) indicates *mercury*. The nitric acid solution is evaporated to a small bulk with sulphuric acid, diluted with cold water and filtered; white residue ($PbSO_4$) indicates *lead*. The filtrate is rendered ammoniacal, blue colour = *copper*; white precipitate ($Bi(HO)_3$) = *bismuth*, confirmed by dissolving in hydrochloric acid and diluting considerably with water (BiOCl). The colour of the filtrate discharged by potassium cyanide (excess); the solution saturated with hydrogen sulphide, a yellow precipitate (CdS) = *cadmium* (confirmation is essential, since a yellow cyanogen derivative may be precipitated at this stage).

Group III. (phosphates absent).—The mixed hydroxides, suspended in water, are warmed with excess of sodium peroxide and filtered. A residue ($Fe_2O_3{\cdot}xH_2O$, which may contain some MnO_2) indicates *iron*. The filtrate is divided into two parts, (i.) boiled with excess of ammonium chloride, white gelatinous precipitate ($Al(OH)_3$) = *aluminium*; (ii.) acidified with dilute acetic acid and lead acetate added, yellow precipitate ($PbCrO_4$) = *chromium*.

Group III. (phosphates present).—If the original solution was acid, this group precipitate may contain phosphates insoluble in neutral or alkaline solutions. The sodium peroxide separation is applied to one-third of the precipitate; the remainder is dissolved in dilute hydrochloric acid, the solution nearly neutralised with pure sodium carbonate, and treated successively with ammonium acetate, acetic acid, and ferric chloride until no further precipitate is produced and the solution is deep red. The mixture is boiled and filtered hot; the filtrate is then examined for the metals of Groups IV. and V., and for magnesium. The precipitate, which is neglected, contains ferric phosphate and basic ferric acetate. Ammonium formate may be used instead of acetate in this separation (Tower, J. Amer. Chem. Soc. 1910, 32, 953).

The phosphoric acid may also be removed by evaporating the filtrate from Group II. to dryness with nitric acid and granulated tin, when an insoluble residue is obtained consisting of metastannic and phosphostannic acids.

Group IV.—The mixed sulphides, washed with hydrogen sulphide water, are dissolved in aqua regia, or hydrochloric acid and potassium chlorate. Excess of sodium hydroxide is added to the solution after expelling excess of acid; the precipitate collected and the filtrate treated with hydrogen sulphide; white precipitate (ZnS) = *zinc*. The precipitated hydroxides are dissolved in hydrochloric acid, excess of ammonium acetate added, and the solution saturated with sulphide. Any black precipitate is removed and the filtrate rendered ammoniacal; pink precipitate (MnS) = *manganese*.

The black precipitate is tested in the borax bead; a brownish-yellow colour indicates *nickel* present and cobalt absent. If the bead is blue (= *cobalt*), the precipitate is dissolved in hydrochloric acid, potassium chlorate added, excess of acid expelled, and the solution *nearly* neutralised with sodium carbonate; excess of potassium cyanide is then added, and the solution boiled in an open dish. An excess of sodium hypochlorite or freshly prepared sodium hypobromite is added to the warm solution; a black precipitate ($Ni_2O_3{\cdot}xH_2O$) = *nickel*; the filtrate contains potassium cobalticyanide ($K_3Co(CN)_6$).

A quicker separation of the Group IV. sulphides may be effected by digesting them with cold dilute hydrochloric acid (1 : 20). This treatment should bring the zinc and manganese into solution, leaving the sulphides of nickel and cobalt undissolved; but it is generally found that appreciable quantities of the latter metals are present in the filtrate. Alternative methods of detecting and separating nickel and cobalt are given under special reactions.

Group V.—Dissolve the washed precipitate in dilute acetic acid, add aqueous potassium chromate; yellow precipitate ($BaCrO_4$) = *barium*: filtrate boiled with concentrated aqueous ammonium sulphate; white precipitate ($SrSO_4$) = *strontium*: final filtrate treated with ammonium oxalate; white precipitate ($CaC_2O_4{\cdot}xH_2O$) = *calcium*. Owing to their close relationship, a sharp separation of the three metals is extremely difficult. The following alternative process has recently been worked out (*v.* Bray, J. Amer. Chem. Soc. 1909, 31, 611).

The group precipitate, which may contain magnesium, is dissolved in 20 c.c. of 30 p.c. acetic acid, solution neutralised with ammonia, 3 c.c. of acetic acid added, diluted to 40 c.c., 10 c.c. of 20 p.c. potassium chromate slowly added, solution boiled for 2 minutes; yellow precipitate ($BaCrO_4$). Three c.c. of ammonia added to filtrate, diluted to 60 c.c., 50 c.c. of alcohol (95 p.c.) added; after 10 minutes yellow precipitate ($SrCrO_4$). Without washing this precipitate, 200 c.c. of water are added to filtrate, the solution boiled, and 40 c.c. of 4 p.c. ammonium oxalate added; after 10 minutes white precipitate (CaC_2O_4). *Magnesium* is precipitated in filtrate as a colourless crystalline precipitate ($Mg(NH_4)PO_4{,}6H_2O$) by adding ammonia and sodium phosphate.

GROUP VI.—A portion of the filtrate from V. examined for *magnesium* (*v. supra*), the remainder evaporated to dryness and ignited to expel ammonium salts. The residue dissolved in a small bulk of water, the solution filtered if necessary, examined by flame test and divided into two parts, (i.) platinic chloride added; yellow crystalline precipitate (K_2PtCl_6) = *potassium*; (ii.) potassium pyroantimonate added; colourless crystalline precipitate ($Na_2H_2Sb_2O_7,6H_2O$) = *sodium*.

GROUP SEPARATION IN THE PRESENCE OF THE RARER METALS.

In the presence of the less commonly occurring elements, the ordinary group separations require, in certain instances, to be modified very considerably. A systematic attempt to deal with this problem has recently been made by A. A. Noyes and his collaborators, to whose original memoirs reference should be made for the exact working details of the necessarily somewhat complicated separations, an outline of which is given below (J. Amer. Chem. Soc. 1907, 29, 137; 1908, 30, 481; 1909, 31, 611).

It will be seen that the greater number of the rarer elements are precipitated by the reagents of Groups II., III., and IV. of the foregoing analytical classification; but in the scheme devised by Noyes, Groups III. and IV. are merged into one, and it is chiefly in this comprehensive group that the additional complications are to be found.

GROUP I.—The precipitate may contain *thallous chloride* and *tungstic acid*. The former is extracted by hot water, any lead separated as sulphate, when the filtrate treated with potassium iodide gives a yellow precipitate (TlI) = *thallium*. The hydrated tungstic acid, precipitated by hydrochloric acid from alkali tungstates, remains in the residue, and may be separated from lead and silver by fusion with sodium carbonate. The aqueous solution of alkali tungstate is boiled with zinc and hydrochloric acid, when the development of a blue colouration = *tungsten*.

GROUP II.—Selenium, tellurium, molybdenum, gold, platinum and its allies, are precipitated by hydrogen sulphide in acid solution. Extraction of the group precipitate with yellow ammonium sulphide carries the greater part of these elements into the tin sub-group, but the separation is not quite sharp, for small but appreciable quantities of molybdenum, gold and the platinum metals remain in the insoluble sulphides of the copper sub-group.

A. *Copper sub-group.*—The precipitate boiled with dilute nitric acid (1 vol. of sp.gr. 1·20 : 2 vols. water) partially dissolves; the solution contains lead, copper, cadmium, and bismuth, while the residue contains mercury, gold, platinum, and a trace of tin. The insoluble portion is oxidised with bromine water, potassium chloride and hydrochloric acid are added and the solution concentrated; a yellow crystalline precipitate (K_2PtCl_6) = *platinum*. The excess of acid is expelled from the solution, which is then rendered alkaline and boiled with excess of oxalic acid; a brownish-black precipitate = *gold*.

B. *Tin sub-group.*—The sulphides are reprecipitated by dilute acid from their solution in ammonium sulphide, and digested for 10 minutes with nearly boiling hydrochloric acid (sp.gr. 1·20); the solution contains tin and antimony, and the residue arsenic and the rarer elements. The residue is dissolved by strong hydrochloric acid and potassium chlorate; the solution concentrated to the crystallising point yields a yellow precipitate (K_2PtCl_6)=*platinum*. The filtrate, treated successively with ammonia and magnesia mixture ($MgCl_2,2NH_4Cl$ with $NH_4{\cdot}OH$), yields a colourless crystalline precipitate ($Mg(NH_4)AsO_4,6H_2O$) = *arsenic*. The filtrate from the double arsenate is evaporated to remove ammonia, and then boiled with oxalic acid, and the brownish-black precipitate (*gold*) extracted with hydrochloric acid to dissolve any co-precipitated tellurous acid. The filtrate from the gold is concentrated and acidified with strong hydrochloric acid, and after removing any precipitated potassium chloride, sodium sulphite (in *slight* excess) is added when a red precipitate = *selenium*. The filtrate from selenium is diluted and treated successively with potassium iodide and solid sodium sulphite (excess); the double iodide, K_2TeI_6, becomes reduced, and a black precipitate = *tellurium*. The final filtrate is boiled with hydrochloric acid to expel sulphur dioxide, and to the cooled solution 10 p.c. potassium thiocyanate and stannous chloride (or a scrap of zinc) are successively added, when a red colouration ($Mo(CNS)_4$) soluble in ether = *molybdenum*.

GROUPS III. and IV.—The filtrate from Group II. is boiled to expel hydrogen sulphide, treated with moderately strong ammonia, the colour of the precipitate being noted, and the ammoniacal mixture heated nearly to boiling and treated with ammonium sulphide, or preferably, in the presence of nickel, with hydrogen sulphide to saturation. In the presence of vanadium the filtrate has a reddish colour, and on adding hydrochloric acid brown vanadium sulphide is precipitated. The acid filtrate is boiled to expel hydrogen sulphide, and treated with ferric chloride and ammonia to precipitate last traces of vanadium. The presence of this metal in the sulphide and ferric hydroxide precipitates is confirmed by dissolving in nitric acid (sp.gr. 1·20), diluting and adding hydrogen peroxide, when an orange-yellow colouration = *vanadium*.

The group precipitate is dissolved in hydrochloric acid (sp.gr. 1·12), adding, if necessary, some nitric acid or bromine water. The solution is then boiled with hydrochloric acid to remove nitric acid, and treated in a platinum dish with 40 p.c. hydrofluoric acid, and evaporated to dryness. An insoluble residue indicates the fluorides of the rare earth metals (thorium, cerium, yttrium, erbium, &c.); the aqueous extract, which contains all the other metals of this analytical group, is evaporated successively with hydrochloric and nitric acids. The insoluble fluorides are decomposed by hot sulphuric acid, and the resulting sulphates of the rare earth metals subjected to special tests for these elements.

The nitric acid solution of the other metals of the group is treated successively with caustic soda solution, dry sodium peroxide, and aqueous sodium carbonate, when a precipitate B and a filtrate A are obtained. This treatment

separates these metals into two sub-groups, and the method is valid even when phosphates are present.

A. *The aluminium sub-group* (may contain sodium glucinate, zincate, aluminate, vanadate, chromate, and peruranate). The solution is acidified with nitric acid (sp.gr. 1·42) and diluted considerably, solid sodium hydrogen carbonate added in moderate excess and the mixture heated in a stoppered bottle. The precipitate (containing zinc, glucinum, and aluminium) is dissolved in hydrochloric acid, and the solution rendered ammoniacal; the zinc remains in solution, while the hydroxides of glucinum and aluminium are precipitated. These hydroxides are dissolved in strong hydrochloric acid, ether (1·5 vols.) is added, and the cooled solution saturated with hydrogen chloride, white crystalline precipitate ($AlCl_3,6H_2O$) = *aluminium*. The ethereal filtrate is evaporated, treated with ammonia, any precipitate dissolved in 10 p.c. sodium hydrogen carbonate, the solution saturated with hydrogen sulphide; the filtrate from any precipitated sulphide is acidified, boiled, and rendered ammoniacal, when a white flocculent precipitate ($Gl(OH)_2$) = *glucinum*.

The filtrate obtained from the first treatment with sodium hydrogen carbonate is acidified with nitric acid, and just neutralised with caustic soda; 2 c.c. of nitric acid (sp.gr. 1·20) and 20 c.c. of 20 p.c. lead nitrate are added; yellow precipitate = *chromium*. The lead is removed with hydrogen sulphide, the excess of gas boiled off, vanadyl salts oxidised to vanadates with bromine, any excess of this reagent being removed by boiling. The solution, after neutralisation with ammonia, is treated successively with 5 c.c. of 30 p.c. acetic acid, 2 grams of ammonium sulphate (or nitrate), and 2 grams of sodium phosphate; the mixture is heated to boiling, when a white precipitate ($UO_2(NH_4)PO_4$) = *uranium*. The final filtrate is rendered ammoniacal, saturated with hydrogen sulphide, acidified with acetic acid, and boiled; dark precipitate = *vanadium*.

B. *The iron-manganese sub-group* (may contain the hydroxides and phosphates of iron, manganese, cobalt, nickel, zinc (traces), titanium, and zirconium, together with calcium, strontium, barium, and magnesium, as carbonates and phosphates). The precipitated hydroxides, &c., are dissolved in hydrochloric acid, the solution evaporated down with strong nitric acid, and treated with 0·5 gram of solid potassium chlorate; brown precipitate = *manganese*. A portion of the filtrate tested for phosphoric acid, when, if present, the remainder is treated with ammonium hydroxide till nearly alkaline, and boiled with ferric chloride and ammonium acetate. The filtrate contains the ordinary metals of Groups III. and IV., together with magnesium; the precipitate consists of the hydroxides, phosphates, and basic acetates of iron, zirconium, titanium, and possibly thallium (tervalent). This precipitate is dissolved in hydrochloric acid (sp.gr. 1·12), and the solution shaken with an equal volume of ether. The ethereal extract contains ferric and thallic chlorides; the hydrochloric acid solution the zirconium and titanium. The latter is evaporated down with sulphuric acid until the hydrogen chloride is expelled, the residue taken up with water and treated with hydrogen peroxide and subsequently with sodium phosphate; orange-yellow colouration (TiO_3) = *titanium*; white flocculent precipitate ($Zr(OH)\cdot PO_4$) = *zirconium*. The final filtrate is reduced with sulphurous acid, when a white flocculent precipitate ($Ti(OH)\cdot PO_4$) confirms *titanium*.

GROUPS V. and VI.—In the presence of lithium it is preferable to precipitate magnesium in the calcium group. The filtrate from Groups III. and IV. is concentrated to 10 c.c. and treated with 30 c.c. of 20 p.c. ammonium carbonate and 30 c.c. of 95 p.c. alcohol. After 30 minutes the precipitation is complete, the magnesium being present as the double carbonate ($MgCO_3$, $(NH_4)_2CO_3,4H_2O$). The treatment of the group precipitate has already been described under Group V. (*v. supra*). The filtrate is evaporated to dryness and ignited. The residue is taken up with 10 c.c. of water, and one-third tested for lithium by adding 0·5 c.c. of 10 p.c. caustic soda and 2 c.c. of 10 p.c. sodium phosphate, heating to boiling and adding 1 c.c. of alcohol, white precipitate (Li_3PO_4) = *lithium*. The filtrate from this phosphate is tested for potassium by adding acetic acid and sodium cobaltinitrite. The remaining two-thirds of the solution, containing the alkali metals, are tested for sodium by potassium pyroantimonate after removing the lithium as fluoride by ammonia and ammonium fluoride.

Examination for Acids.

Although it is not possible to separate the acidic radicles into a limited number of groups, each having a group reagent, yet the reactions may be divided into (i.) preliminary tests made on the original solution or substance; and (ii.) systematic tests made on suitably prepared solutions. The reactions may be conveniently carried out in the following order :—

I. *Preliminary tests* (compare dry reactions).

1. The original substance or solution is warmed with dilute hydrochloric or sulphuric acid. A gas is evolved, carbon dioxide, turning lime water milky = *carbonate*; sulphur dioxide = *sulphite*; hydrogen sulphide, blackening lead acetate paper = *sulphide* (not all); nitrous fumes = *nitrite*; hydrogen cyanide, odour of bitter almonds = *cyanide*.

2. The original substance or solution warmed slowly with strong solution of sodium dichromate slightly acidified, carbon dioxide evolved, confirms *carbonate* in presence of sulphite.

3. *Heating with concentrated sulphuric acid.*—The foregoing gases may be evolved, and in addition the following :—

(*a*) *Colourless*:

Fuming acid gas etching glass = *fluoride*; fuming acid gas not etching = *chloride*; odour of vinegar = *acetate*; carbon monoxide, blue flame = *formate, ferrocyanide*; carbon monoxide and dioxide = *oxalate*; sulphur dioxide and sulphur sublimate = *thiosulphate*.

(*b*) *Colour.*

Orange vapour, bromine = *bromide*; violet vapour and hydrogen sulphide = *iodide*; nitrous fumes = *nitrite, nitrate*; oxides of carbon and sulphur with charring = *tartrate, citrate, malate*; yellow explosive chlorine oxide = *chlorate*.

4. *Heating with alcohol and concentrated*

sulphuric acid, green flame = *borate*. Before performing this test chlorates must be decomposed by igniting the original substance, otherwise an explosion may result.

5. *Heating with concentrated sulphuric acid and sand*, a colourless gas (SiF_4), giving a gelatinous precipitate on moist rod, confirms *fluoride*.

II. *Systematic tests.*—Before testing a solution for acids, boil with excess of pure sodium carbonate to remove heavy metals, filter, and carefully neutralise with nitric acid.

1. *Barium chloride* in neutral solution yields: (α) a white precipitate, insoluble in hydrochloric acid = *sulphate, silicofluoride*; (β) a white precipitate, soluble in hydrochloric acid = *sulphite, carbonate, phosphate, oxalate, borate, fluoride, silicate, tartrate*; (γ) a yellow precipitate = *chromate*.

2. To a portion of the neutral solution add *calcium chloride* in excess, allow to stand for some time with occasional shaking, and filter. A white precipitate (α) insoluble in acetic acid = *oxalate* (*sulphate* in strong solutions); (β) soluble in acetic acid = *phosphate, borate*, and other acids precipitated by barium chloride.

Calcium *tartrate* after washing is soluble in potash, and is re-precipitated on diluting and boiling.

The filtrate from the precipitate in the cold is boiled for some time and filtered hot; a white precipitate = *citrate* (*malate* in strong solutions). The filtrate from this precipitate is allowed to cool and then mixed with excess of alcohol; a white precipitate = *succinate, malate*.

3. *Silver nitrate* in neutral solution yields:

(α) A precipitate soluble in nitric acid.

(1) White = *oxalate, borate, tartrate, benzoate*, &c.

(2) Yellow = *phosphate, arsenite*.

(3) Brick-red = *arsenate*.

(4) Dark-red = *chromate*.

(β) A precipitate insoluble in nitric acid.

Soluble in ammonia: White = *chloride* (*hypochlorite*), *cyanide, thiocyanate*; yellowish-white = *bromide*; orange-red = *ferricyanide*; white = *ferrocyanide* (sparingly soluble).

Insoluble in ammonia: Yellow = *iodide*; black = *sulphide*.

4. *Ferric chloride* in neutral solutions yields:

(α) A colouration: blood-red = *acetate, formate* (precipitate on boiling), *thiocyanate* (no precipitate on boiling); violet = *salicylate, thiosulphate* (fugitive); bluish-black = *tannate, gallate*; greenish-brown = *ferricyanide* (dark-blue precipitate on adding stannous chloride).

(β) A precipitate: buff = *benzoate, carbonate*; reddish-brown = *succinate*; white = *phosphate*; black = *sulphide*; bluish- or greenish-black = *tannate, gallate*.

Sulphur acids. (1) Detect *sulphate* by barium chloride, and *sulphide* by lead acetate, &c. Make part of the solution slightly alkaline with potash, add zinc sulphate in considerable excess, and filter. Test one part of the filtrate for *thiosulphate* by means of hydrochloric acid; to the other part add acetic acid till *faintly* acid, sodium nitroprusside in small quantity, and potassium ferrocyanide; a pink precipitate indicates a *sulphite*.

(2) Separation of soluble sulphates, sulphites, sulphides, and thiosulphates in neutral solution. Precipitate *sulphide* as CdS, PbS, or ZnS by adding cadmium carbonate or lead carbonate sludge or zinc chloride solution. Add strontium nitrate and leave for 12 hours; the precipitated strontium *sulphate* and *sulphite* separated by hydrochloric acid, the filtrate contains the *thiosulphate*, decomposed by strong hydrochloric acid, giving sulphur and sulphur dioxide (Autenrieth and Windaus, Zeitsch. anal. Chem. 1898, 37, 295).

Chloride, bromide, and iodide. (1) Place the substance in a small flask connected with a small bulb U-tube containing a little starch paste and placed in a beaker of water. Add water and ferric sulphate solution to the substance in the flask, and heat to boiling. If iodine is present, the starch paste becomes blue. Remove the cork, boil with fresh additions of ferric sulphate till all iodine is expelled. Now add a few crystals of potassium permanganate, connect with a bulb tube containing chloroform, and again boil. If bromine is present, the chloroform is coloured brown. Boil with addition of more permanganate until all bromine is expelled, filter and test filtrate for chlorine (Hart, Amer. Chem. J. 1884, 6, 346).

(2) After iodine has been detected by means of nitrogen oxides in sulphuric acid, evaporate part of the solution to dryness with sodium carbonate, fuse with ten times its weight of potassium dichromate till all iodine is expelled, place in a small dry retort, and heat with strong sulphuric acid. Part of the distillate is agitated with water and carbon disulphide; if bromine is present, the latter becomes orange-red. The remainder of the distillate is neutralised with ammonia, and tested for chromic acid by acidifying with acetic acid and adding lead acetate. The presence of chromic acid indicates the presence of chlorine in the original substance.

(3) A neutral solution of the three halides is treated with potassium iodate and dilute acetic acid; as iodine is liberated, more iodate is added and the solution boiled until all the iodine is eliminated. The solution is mixed with half its volume of 5*N*-nitric acid, bromine is evolved and the solution boiled till colourless. A little potassium iodide added to destroy the iodate in excess, and the solution boiled till colourless, then an equal volume of strong nitric acid and a few drops of silver nitrate are added, when a white precipitate indicates a chloride: The strong nitric acid holds in solution any trace of silver iodate. If thiocyanic acid is present, the test for iodine must be made in a small portion of the original solution, adding sodium acetate as well as acetic acid to depress the dissociation of the latter (Benedikt and Snell, J. Amer. Chem. Soc. 1903, 25, 809).

Other acids must be detected by special tests. Iodine, and ferrocyanides and ferricyanides must be removed before testing for nitrates.

To remove iodine, ferrocyanic, ferricyanic, and thiocyanic acids, add excess of a mixture of cupric and ferrous sulphates, and filter. To remove excess of copper and iron (which is not always necessary) heat to boiling, add slight excess of *pure* caustic potash or soda, and filter.

To remove bromine and iodine, acidify with dilute sulphuric acid, and boil with successive additions of potassium permanganate until the liquid has a faint permanent pink tinge; filter.

To remove hypochlorous and nitrous acids, acidify with dilute sulphuric acid, and boil. Nitrous acid can also be decomposed by boiling with a strong solution of ammonium chloride.

For an alternative classification of the acidic radicles into analytical groups, compare T. Milobendski (J. Russ. Phys. Chem. Soc. 1909, 41, 1301).

Special Reactions.

In the following lists only the most characteristic and useful reactions have been given; negative reactions, and others not particularly characteristic, have, as a rule, been omitted (*see also* Dry reactions).

Metals.

The metals are arranged in the order of their occurrence in the systematic separation.

Silver.

Hydrochloric acid, a white precipitate (AgCl), insoluble in hot water and in nitric acid; soluble in ammonia and reprecipitated by nitric acid in excess. *Potassium chromate*, a dark-red precipitate (Ag_2CrO_4); soluble in mineral acids and decomposed by caustic alkalis. *Potassium cyanide*, white precipitate (AgCN) soluble in excess to $KAg(CN)_2$.

Lead.

Hydrochloric acid, a white precipitate ($PbCl_2$), soluble in hot water, from which it crystallises on cooling; insoluble in ammonia. *Hydrogen sulphide*, a black precipitate (PbS), insoluble in ammonium sulphide (in presence of hydrogen halides, intermediate red compounds are produced, *e.g.* $PbS,4PbI_2$, J. Amer. Chem. Soc. 1895, 17, 511; 1901, 23, 680); soluble in nitric acid. *Sulphuric acid*, a white precipitate ($PbSO_4$), soluble in hot hydrochloric acid; insoluble in dilute sulphuric acid; soluble in ammonium acetate (Noyes and Whitcomb, J. Amer. Chem. Soc. 1905, 27, 747). *Potassium chromate*, yellow precipitate ($PbCrO_4$), insoluble in acetic acid; soluble in potassium hydroxide.

Thallium.

Hydrochloric acid, white precipitate (TlCl), only slightly soluble in hot water. *Potassium iodide*, pale-yellow precipitate (TlI), even in dilute solutions. *Sulphuric acid*, no precipitate (diff. from Pb). *Sodium cobaltinitrite* gives red crystalline precipitate ($Tl_3Co(NO_2)_6$) (J. Russ. Phys. Chem. Soc. 1910, 42, 94).

Tungsten.

Hydrochloric acid, a yellowish-white precipitate (H_2WO_4), insoluble in excess of the dilute acid; soluble in the concentrated acid and in tartaric acid; fragments of zinc added to this solution produce a blue colouration. *Stannous chloride*, a yellow precipitate, which becomes blue if mixed with hydrochloric acid and heated. *Ammonium sulphide*, no precipitate with sodium tungstate, but on acidifying, light-brown precipitate (WS_3), insoluble in hydrochloric acids, soluble in ammonium sulphide.

Mercury.

Mercurous compounds. Hydrochloric acid, white precipitate (Hg_2Cl_2), insoluble in hot water; insoluble in ammonia, but blackened (NH_2Hg_2Cl). *Stannous chloride*, grey precipitate (Hg). *Metallic copper*, becomes coated with mercury, which can be sublimed.

Mercuric compounds. Hydrogen sulphide, white precipitate, becoming yellow, red, and then black (HgS); insoluble in ammonium sulphide; appreciably soluble in alkali sulphides ($Hg(SNa)_2$), insoluble in nitric acid; soluble in aqua regia. *Stannous chloride*, white precipitate (Hg_2Cl_2), becoming grey (Hg) with excess of the reagent. *Potassium iodide*, scarlet precipitate (HgI_2), soluble in excess. *Metallic copper*, as mercurous salts.

Bismuth.

Hydrogen sulphide, brown precipitate (Bi_2S_3), insoluble in ammonium sulphide; soluble in nitric acid. *Ammonia*, white precipitate ($Bi(HO)_3$), soluble in hydrochloric acid. *Water* in large excess (with previous addition of ammonium chloride if chlorides are absent), white precipitate (BiOCl), soluble in hydrochloric acid; insoluble in tartaric acid. *Reducing agents* (sodium stannite, hypophosphites, hydrosulphites, formaldehyde in alkaline solution) reduce bismuth compounds to elemental bismuth.

Copper.

Hydrogen sulphide, black precipitate (CuS), insoluble in ammonium sulphide and in dilute sulphuric acid; soluble in nitric acid and in potassium cyanide. *Ammonia*, blue precipitate, soluble in excess to dark-blue solution. *Potassium ferrocyanide*, chocolate-brown precipitate, insoluble in dilute acids; in very dilute solutions colouration only; decomposed by sodium hydroxide, yielding blue copper hydroxide.

Cadmium.

Hydrogen sulphide, yellow precipitate (CdS), insoluble in ammonium sulphide and potassium cyanide; soluble in nitric acid and hot dilute sulphuric acid. *Ammonia*, white precipitate (CdH_2O_2), readily soluble in excess. *Caustic potash* or *soda*, white precipitate (CdH_2O_2) insoluble in excess.

Tin.

Stannous compounds. Hydrogen sulphide, dark-brown precipitate (SnS), soluble in yellow but not in colourless ammonium sulphide. *Mercuric chloride*, white precipitate (Hg_2Cl_2), becoming grey (Hg).

Stannic compounds. Hydrogen sulphide, yellow precipitate (SnS_2), soluble in ammonium sulphide; appreciably soluble in ammonium carbonate (Ber. 1894, 27, 2739); soluble in concentrated hydrochloric acid; dissolves in aqueous caustic soda. *Stannic chloride*, boiled with copper becomes stannous chloride. When *zinc* and *platinum* are placed in the solution, no black stain on the platinum; crystals of tin on the zinc.

Antimony.

Hydrogen sulphide, orange precipitate (Sb_2S_3), soluble in ammonium sulphide and in concentrated hydrochloric acid; insoluble in ammonium carbonate. *Water* in excess (with ammonium chloride if chlorides are absent), white precipitate (SbOCl), soluble in hydrochloric acid and in tartaric acid. *Zinc* and *platinum*, a black stain on the platinum (Sb), soluble in nitric acid and in ammonium sulphide.

Arsenic.

Hydrogen sulphide, yellow precipitate, soluble in ammonium sulphide and in ammonium carbonate; insoluble in concentrated hydrochloric acid. *Metallic copper*, boiled with the liquid after acidifying with hydrochloric acid, is covered with a shining grey deposit (As_2Cu_3), which, when

heated in a tube, yields a sublimate of arsenious oxide (Reinsch's test) (Clark, Chem. Soc. Trans. 1893, 63, 884, 886). *Nascent hydrogen* produced from zinc and dilute sulphuric acid reduces arsenic compounds to volatile arsine (AsH_3), which decomposes on gently heating, giving an arsenic deposit soluble in aqueous hypochlorites. Antimony compounds under these conditions also give a black deposit (antimony), insoluble in hypochlorites (Marsh's test). Zinc and caustic soda reduce arsenic compounds, liberating arsine, which produces a yellow-to-brown stain on mercuric chloride paper (Gutzeit's test, Chem. Soc. Trans. 1901, 79, 715).

Arsenites. Ammonio-silver nitrate, yellow precipitate (Ag_3AsO_3), soluble in nitric acid and ammonia. *Ammonio-cupric sulphate*, bright-green precipitate ($CuHAsO_3$), turns red by boiling with caustic soda.

Arsenates. Ammonio-silver nitrate, brick-red precipitate (Ag_3AsO_4), soluble in nitric acid and ammonia. *Ammonium chloride, ammonia*, and *magnesium sulphate*, white crystalline precipitate (NH_4MgAsO_4). *Ammonio-cupric sulphate*, pale-blue precipitate, turned black by boiling with caustic soda.

When arsenic acid or arsenates are present, they should be reduced by heating with sulphurous acid or ammonium iodide or hydriodic acid (Bull. Soc. chim. Belg. 1909, 23, 88) before applying hydrogen sulphide or Reinsch's test (Usher and Travers, Chem. Soc. Trans. 1905, 87, 1370).

Platinum.

Hydrogen sulphide, brown precipitate (PtS_2) on heating, soluble in ammonium sulphide. *Ammonium chloride* or *potassium chloride*, yellow crystalline precipitate (M_2PtCl_6), less soluble in presence of alcohol. *Potassium iodide*, in dilute solution red colouration (K_2PtI_6), very delicate test. *Stannous chloride*, in dilute solution, brownish-red colouration, delicate test.

Palladium.

Hydrogen sulphide, black precipitate (PdS), insoluble in ammonium sulphide; soluble in hot hydrochloric acid and in aqua regia. *Potassium iodide*, black precipitate (PdI_2), somewhat soluble in excess. *Mercuric cyanide*, yellowish white, gelatinous precipitate ($PdCy_2$), readily soluble in ammonia. *Ammonium chloride*, no precipitate (diff. from Pt); on addition of chlorine water, orange precipitate ($(NH_4)_2PdCl_6$). *Potassium chloride*, precipitate ($2KCl{\cdot}PdCl_2$) only in very concentrated solutions.

Iridium.

Hydrogen sulphide, decolourisation followed by brown precipitate (Ir_2S_3), soluble in ammonium sulphide. *Caustic potash*, a greenish colouration which, on heating with exposure to air, changes slowly to azure blue (diff. from Pt). *Ammonium chloride* or *potassium chloride*, dark-brown or red precipitate (double chloride), insoluble in a saturated solution of the precipitant. Both salts become olive green with potassium nitrite and other reducing agents, especially in hot solutions. *Strong sulphuric acid* and *ammonium nitrate*, on heating, blue colouration.

Osmium.

Hydrogen sulphide, in acid but not in neutral solution, black precipitate (OsS_4), insoluble in ammonium sulphide. *Nitric acid* on boiling oxidises osmium compounds to osmic tetroxide (OsO_4), characteristic odour and yellow solution in caustic soda.

Ruthenium.

Hydrogen sulphide, blue solution followed by brown precipitate of ruthenium sulphide. *Sodium thiosulphate* in ammoniacal solution to dilute solutions of ruthenium, a purplish-red colouration. *Zinc* reduces $RuCl_3$, giving a blue solution and then precipitating ruthenium.

Rhodium.

Hydrogen sulphide, on warming, black precipitate (Rh_2S_3), insoluble in ammonium sulphide; soluble in boiling nitric acid. *Potassium nitrite*, warmed with sodium rhodium chloride, gives orange-yellow precipitate ($K_3Rh(NO_2)_6$).

Gold.

Hydrogen sulphide, black precipitate (Au_2S_3) in cold, brown precipitate (Au_2S) in hot, solution; soluble in yellow ammonium sulphide. *Oxalic acid* or *ferrous sulphate*, brown or purple precipitate, yellow and lustrous when rubbed. *Stannous* and *stannic chlorides*, purplish precipitate, insoluble in hydrochloric acid. *Hydrogen peroxide*, in very dilute alkaline solution, liberates finely divided gold having a beautiful blue shimmer.

Molybdenum.

Hydrogen sulphide, brownish-black precipitate (MoS_3) on heating, soluble in ammonium sulphide. *Sodium phosphate*, in presence of nitric acid, yellow precipitate on heating, soluble in ammonia and in excess of the alkaline phosphate. *Potassium thiocyanate* and zinc or stannous chloride, red colouration due to $Mo(CNS)_4$ soluble in ether. *Concentrated sulphuric acid*, when strongly heated with molybdenum compounds, develops a deep-blue colouration. *Phenylhydrazine*, in 50 p.c. acetic acid, red colouration (Ber. 1903, 36, 512).

Selenium.

Hydrogen sulphide, yellow precipitate, becoming dark on heating, soluble in ammonium sulphide. *Sulphurous acid*, in presence of hydrochloric acid, a red precipitate, which becomes grey on heating, and is soluble in potassium cyanide. *Stannous chloride* and other reducing agents behave in a similar manner. *Barium chloride*, (i.) white precipitate ($BaSeO_3$), soluble in dilute hydrochloric acid; (ii.) white precipitate ($BaSeO_4$), insoluble in dilute hydrochloric acid; soluble in the strong acid, evolving chlorine. *Concentrated sulphuric acid*, green colouration.

Tellurium.

Hydrogen sulphide, brown precipitate (TeS_2) at once from tellurites, but from tellurates only after boiling with hydrochloric acid. *Potassium iodide*, to tellurite in acid solution, black precipitate (TeI_4). *Reducing agents* ($SnCl_2$, Zn), black precipitate (Te). *Concentrated sulphuric acid*, carmine colouration.

Aluminium.

Ammonia, white gelatinous precipitate (AlH_3O_3), insoluble in excess and in ammonium carbonate; soluble in acids. *Caustic potash* or *soda*, white gelatinous precipitate (AlH_3O_3), soluble in excess; reprecipitated on adding ammonium chloride and heating.

Chromium.

Chromic salts. Ammonia, greenish or purplish precipitate (CrH_3O_3), soluble in acids; insoluble in ammonium carbonate. *Caustic*

potash or *soda*, green precipitate (CrH_3O_3), soluble in excess, but reprecipitated on boiling.

Chromates. Hydrogen sulphide in acid solution, reduction to chromic salt with change of colour to green. *Lead acetate*, bright yellow precipitate ($PbCrO_4$), insoluble in acetic acid. *Silver nitrate*, dark-red precipitate (Ag_2CrO_4), soluble in nitric acid.

Iron.

Ferrous salts. Ammonium sulphide, black precipitate (FeS), soluble in acids. *Ammonia* or *caustic potash* or *soda*, white precipitate, rapidly becoming green and then brown. *Potassium ferrocyanide*, white precipitate, gradually becoming dark blue. *Potassium ferricyanide*, dark-blue precipitate ($Fe_3(FeCy_6)_2$). *Potassium thiocyanate*, no reaction.

Ferric salts. Ammonium sulphide, black precipitate ($2FeS + S$, or Fe_2S_3), soluble in acids. *Ammonia* or *caustic potash* or *soda*, reddish-brown precipitate (FeH_3O_3), soluble in acids. *Potassium ferrocyanide*, dark-blue precipitate ($Fe_4(FeCy_6)_3$), insoluble in dilute acids. *Potassium ferricyanide*, no precipitate; greenish-brown colouration. *Potassium thiocyanate*, blood-red colouration; not affected by boiling or by hydrochloric acid.

Thorium.

Ammonia, *caustic soda*, or *potash*, white gelatinous precipitate ($Th(OH)_4$), insoluble in excess. *Ammonium* or *sodium carbonate*, white precipitate, basic carbonate; soluble in excess. *Oxalic acid*, white precipitate ($Th(C_2O_4)_2,2H_2O$), insoluble in excess and insoluble in mineral acids, but soluble in ammonium oxalate. *Potassium fluoride* or *hydrofluoric acid*, white precipitate (ThF_4). *Potassium sulphate*, white crystalline precipitate ($2K_2SO_4,Th(SO_4)_2,2H_2O$).

Cerium.

Ammonia, white precipitate of basic salt, insoluble in excess. *Caustic potash* or *soda*, white precipitate ($Ce(OH)_3$), insoluble in excess; becomes yellow when exposed to air. *Oxalic acid*, white precipitate ($Ce_2(C_2O_4)_3$), insoluble in excess, but soluble in a large quantity of hydrochloric acid. *Potassium sulphate*, white precipitate even in somewhat acid solutions ($CeK_3(SO_4)_3$), insoluble in saturated solution of potassium sulphate. *Hydrogen peroxide*, in ammoniacal solution, orange-brown precipitate.

Glucinum.

Ammonia, white precipitate (GlH_2O_2), insoluble in excess. *Caustic potash* or *soda*, the same precipitate, soluble in excess, but reprecipitated on boiling (diff. from Al). *Ammonium carbonate*, white precipitate, easily soluble in excess (diff. from Al).

Glacial acetic acid dissolves $Gl(OH)_2$ or $GlCO_3$, and the residue, after evaporating to dryness, is the basic acetate ($Gl_4O(CH_3{\cdot}CO_2)_6$), readily soluble in chloroform, ether, acetone, the alcohols, and other organic media; dissolves unchanged in glacial acetic acid; it melts at 283°–284°, and can be sublimed without decomposition. *Sodium hydrogen carbonate*, 10 p.c. dissolves $Gl(OH)_2$; dilution to 1 p.c. causes reprecipitation.

Uranium.

Ammonia, *caustic potash*, or *soda*, yellow precipitate, insoluble in excess, but readily soluble in ammonium carbonate. *Ammonium sulphide*, brown precipitate, readily soluble in ammonium carbonate. *Potassium ferrocyanide*, chocolate-brown precipitate, readily decomposed by alkalis, yielding yellow alkali diuranates.

Titanium.

Ammonia, *caustic potash*, or *soda*, or *ammonium sulphide*, white precipitate (H_2TiO_3), insoluble in excess; soluble in dilute sulphuric and hydrochloric acids. *Potassium ferrocyanide*, dark-brown precipitate. *Sodium thiosulphate*, complete precipitation on boiling. *Hydrogen peroxide*, to a slightly acid solution of titanium sulphate; orange-red colouration; weakened by fluorides. *Reducing agents* ($SnCl_2$ or Zn and HCl) produce a violet colouration ($TiCl_3$).

Catechol added to dilute solutions of titanic or titanous salts, yellowish-orange colouration, very delicate test, but interfered with by mineral acids or alkalis (Ber. 1909, 42, 4341).

Zirconium.

Ammonia, *ammonium sulphide*, *caustic soda*, white gelatinous precipitate, dissolving in dilute acid, but less readily after boiling; precipitation prevented by tartaric acid. *Oxalic acid*, white precipitate ($Zr(C_2O_4)_2$), readily soluble in ammonium oxalate or in excess of oxalic acid. *Hydrogen peroxide*, white milky precipitate (Zr_2O_5), evolving chlorine when boiled with hydrochloric acid. *Turmeric paper*, moistened with acid solution of zirconium salt, becomes reddish-brown on drying.

Zinc.

Ammonium sulphide, white precipitate (ZnS), soluble in dilute hydrochloric acid; insoluble in acetic acid and in alkalis. *Caustic potash* or *soda*, white precipitate (ZnH_2O_2), soluble in excess. *Potassium ferrocyanide*, white precipitate, insoluble in dilute hydrochloric acid (Zn_2FeCy_6).

Manganese.

Ammonium sulphide, pink precipitate (MnS), soluble in dilute hydrochloric acid and in acetic acid. *Caustic potash* or *soda*, white precipitate (MnH_2O_2), insoluble in excess, becoming brown on exposure to air. Boiled with dilute *nitric acid* and *lead peroxide* (in absence of chlorine), a purplish crimson solution of permanganic acid.

Nickel.

Ammonium sulphide, black precipitate (NiS), somewhat soluble in excess; insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Caustic potash* or *soda*, pale-green precipitate (NiH_2O_2), insoluble in excess. *Potassium cyanide*, precipitate ($NiCy_2$), soluble in excess, forming $NiCy_2,2KCy$, which is not altered when boiled with exposure to air. This solution, heated with excess of sodium hypochlorite solution, or mixed with bromine in the cold, yields a precipitate of black nickelic hydroxide (NiH_3O_3). *Dimethylglyoxime* ($CH_3{\cdot}C(NOH){\cdot}C(NOH){\cdot}CH_3$) (Tschugaeff, Ber. 1905, 38, 2520), added to ammoniacal or acetic acid solution of nickel salts, scarlet precipitate (distinction from cobalt). *Dicyanodiamidine* (H. Grossmann and W. Heilborn, Ber. 1908, 41, 1878) added to ammoniacal solutions of cobalt and nickel salts containing excess of sucrose, yellow crystalline precipitate ($Ni(N_4H_5C_2O)_2,2H_2O$), the presence of cobalt indicated by the reddish-violet colour of the solution.

Cobalt.

Ammonium sulphide, black precipitate (CoS), insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Caustic potash*, pale-blue

precipitate (CoH_2O_2), slightly soluble in excess, forming a blue solution. *Potassium cyanide*, precipitate ($CoCy_2$), soluble in excess, forming $CoCy_2,4KCy$, and when this solution is boiled with exposure to air it is changed to K_3CoCy_6, which is not precipitated by sodium hypochlorite or bromine. *Potassium nitrite* to dilute acetic acid solutions, yellow crystalline precipitate ($K_3Co(NO_2)_6$). *Nitroso-β-naphthol* $NO{\cdot}C_{10}H_6{\cdot}OH$ (Ilinski and Knorre, Ber. 18, 699) dissolved in dilute acetic acid added to feebly acid solutions of cobalt and nickel, brick-red precipitate ($Co(NO{\cdot}C_{10}H_6{\cdot}O)_3$); solution examined for nickel (Chaplin, J. Amer. Chem. Soc. 1907, 29, 1029).

Vanadium.

Ammonium sulphide, dark-brown solution, which when acidified yields a brown precipitate (V_2S_4). *Ammonium chloride*, white precipitate of ammonium meta-vanadate (NH_4VO_3). *Potassium ferrocyanide*, in acid solution, a green precipitate. If a solution of an alkaline vanadate is agitated with *hydrogen peroxide* and *ether*, the solution acquires a deep purplish-red colour, but the ether remains colourless. *Mild reducing agents* (SO_2, H_2S, HBr, alcohol, &c.) reduce vanadates in acid solutions to blue divanadyl salts. *Strong reducing agents* (zinc and aluminium with acids) produce a series of colour changes—blue, green, and violet.

Columbium.

Hydrogen fluoride and *potassium fluoride* produce potassium columbo-fluoride, which when boiled in aqueous solution yields potassium columbium oxyfluoride (K_2CbOF_5,H_2O) (solubility 1 in 12·5 cold water). *Mineral acids*, partial precipitation of columbic acid from alkali columbates: *zinc* and *acid*, blue colouration, turning brown; *potassium ferrocyanide*, greyish-green precipitate.

Tantalum.

Hydrogen fluoride and *potassium fluoride* produce potassium tantalofluoride (K_2TaF_7) (solubility 1 in 154 cold water), separating in colourless needles. *Mineral acids*, white precipitate of tantalic acid. *Potassium ferrocyanide*, reddish-brown precipitate (*v.* Weiss and Landecker, Zeitsch. anorg. Chem. 1909, 64, 65).

Calcium.

Ammonium carbonate, white precipitate ($CaCO_3$), soluble in acids. *Sulphuric acid*, white precipitate only in very concentrated solutions. *Ammonium oxalate*, white precipitate (CaC_2O_4), insoluble in acetic and oxalic acids, but soluble in hydrochloric acid.

Strontium.

Ammonium carbonate, white precipitate, soluble in acids ($SrCO_3$). *Ammonium sulphate*, white precipitate, especially on boiling. *Ammonium oxalate*, white precipitate (SrC_2O_4), soluble in hydrochloric acid; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate*, white precipitate ($SrSO_4$), forming slowly.

Barium.

Ammonium carbonate, white precipitate ($BaCO_3$), soluble in acids. *Ammonium oxalate*, white precipitate (BaC_2O_4), soluble in hydrochloric acid; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate*, an immediate white precipitate, insoluble in acids and alkalis. *Potassium chromate*, yellow precipitate ($BaCrO_4$), insoluble in acetic acid.

Magnesium.

Sodium phosphate, in presence of ammonia and ammonium chloride, white precipitate, rapidly becoming crystalline ($NH_4MgPO_4{\cdot}6H_2O$). Forms slowly in dilute solutions, formation being accelerated by agitation and by rubbing the sides of the beaker with a glass rod; soluble in acids.

Potassium.

Chloroplatinic acid H_2PtCl_6, yellow crystalline precipitate (K_2PtCl_6), somewhat soluble in water; insoluble in alcohol. *Sodium hydrogen tartrate*, in neutral or feebly acid solutions, a white crystalline precipitate ($KHC_4H_4O_6$), forming slowly in dilute solutions. If the solution contains free mineral acids, nearly neutralise with soda and add sodium acetate.

Sodium cobaltinitrite in acetic acid solution, yellow precipitate ($K_2NaCo(NO_2)_6$). ● *Sodium 1-amino-β-naphthol-6-sulphonate* (eikonogen) in 5–10 p.c. solutions, crystalline precipitate ($KSO_3{\cdot}C_{10}H_5(NH_2){\cdot}OH$); negative results with ammonium and magnesium salts (Alvarez, Chem. Soc. Abstr. 1905, ii. 355).

Ammonium.

Ammonium salts are readily volatile. *Heated with lime, caustic potash*, or *soda*, ammonia gas is given off, and is recognised by its smell and its action on test paper.

Chloroplatinic acid, yellow crystalline precipitate ($(NH_4)_2PtCl_6$), slightly soluble in water; insoluble in alcohol. *Sodium hydrogen tartrate*, white crystalline precipitate ($NH_4HC_4H_4O_6$), forming slowly in dilute solutions.

Nessler's reagent (K_2HgI_2 and KOH), brownish-red precipitate or colouration (NHg_2I,H_2O), very delicate test.

Sodium.

Flame colouration, intense yellow.

Although all sodium salts are more or less soluble, some dissolve only sparingly, *e.g.* sodium oxalate and sodium α-naphthylamine-8-sulphonate.

Potassium pyroantimonate, white crystalline precipitate ($Na_2H_2Sb_2O_7{\cdot}6H_2O$) (J. Amer. Chem. Soc. 1909, 31, 634); from neutral or slightly alkaline solutions.

Dihydroxytartaric acid, colourless precipitate ($CO_2Na.C(OH)_2{\cdot}C(OH)_2{\cdot}CO_2Na$) (Fenton, Chem. Soc. Trans. 1895, 67, 48). *Solution of bismuth nitrate in 50 p.c. potassium nitrite containing cæsium nitrite*, yellow crystalline precipitate ($5Bi(NO_2)_3,9CsNO_2,6NaNO_2$); very delicate test, not interfered with by lithium and metals of alkaline earths (Ball, Chem. Soc. Trans. 1909, 95, 2126). Sodium chloride, obtained by slow evaporation of a solution acidified with hydrochloric acid, crystallises in distinct cubes.

Lithium.

Chloroplatinic acid, no precipitate.

Sodium phosphate, in alkaline solution; white precipitate (Li_3PO_4), soluble in hydrochloric acid, not reprecipitated by ammonia except on boiling. Lithium chloride is soluble in ethyl or amyl alcohol, and in pyridine. *Ammonium hydrogen fluoride*, white precipitate (LiF).

Cæsium.

Flame colouration, violet.

Chloroplatinic acid, yellow crystalline precipitate (Cs_2PtCl_6), insoluble in boiling water, *Tartaric acid*, crystalline precipitate, somewhat soluble in water. *Stannic chloride*, white

precipitate (Cs_2SnCl_6). *Lead chloride dissolved in chlorine water*, yellow precipitate (Cs_2PbCl_6). Cæsium carbonate is soluble in alcohol (diff. from K, Rb).

Rubidium.

Flame colouration, violet.

Chloroplatinic acid, yellow crystalline precipitate (Rb_2PtCl_6), insoluble in boiling water. *Tartaric acid*, white crystalline precipitate, less soluble than the cæsium compound (Reactions of Cs and Rb, *v.* Wells, Amer. J. Sci. [3] 43, 17 and 46, 186, and 265).

Acid Radicles.

The acid radicles are arranged partly in the order of the systematic separation and partly with a view to bring together those acids which are commonly associated or which resemble one another in their reactions. In all cases, unless otherwise specified, it is important that the solution should be neutral.

Sulphates.

Barium chloride, white precipitate ($BaSO_4$), insoluble in acids and alkalis.

Sulphites.

Hydrochloric acid, sulphur dioxide evolved, but no sulphur precipitated. *Barium chloride*, white precipitate ($BaSO_3$), soluble in hydrochloric acid. *Iodine solution*, sulphites are converted into sulphates. Neutralise, then *slightly* acidify with acetic acid; add excess of *zinc sulphate*, a small quantity of *sodium nitroprusside* and *potassium ferrocyanide*. The precipitate of zinc ferrocyanide has a pink colour.

Strontium chloride, white precipitate ($SrSO_3$), different from thiosulphate SrS_2O_3, being much more soluble.

Hyposulphites ('hydrosulphites,' *e.g.* $Na_2S_2O_4$, $2H_2O$) owe their technical application to their reducing action on indigotin and its sulphonic acids—the colour is discharged (indigo-white). *Silver nitrate*, black precipitate (Ag). *Mercuric chloride*, black precipitate (Hg). *Copper sulphate*, reddish precipitate (Cu and Cu_2H_2), in very dilute solution, colloidal copper.

Thiosulphates.

Hydrochloric acid, sulphur dioxide evolved and sulphur precipitated. *Silver nitrate*, white precipitate ($Ag_2S_2O_3$), rapidly changing to black (Ag_2S), soluble in excess of alkaline thiosulphate, forming a much more stable solution. With *sodium nitroprusside*, *zinc sulphate*, and *potassium ferrocyanide*, the precipitate is white. *Iodine solution* converts soluble thiosulphates into tetrathionates, which give no precipitate with barium chloride. *Ferric chloride*, transient violet colouration ($Fe_2(S_2O_3)_3$).

Persulphates (*e.g.* $K_2S_2O_8$).

The dry salts evolve oxygen on heating. *Barium chloride*, no precipitate in the cold, on warming oxygen evolved and $BaSO_4$ precipitated. *Silver nitrate*, black precipitate (silver peroxide). *Other metallic salts* (Pb, Mn, Co, and Ni) yield their hydrated peroxides.

Monopersulphuric acid (*Caro's acid*) $HO{\cdot}SO_2{\cdot}O{\cdot}OH$, produced by adding a persulphate to cold concentrated sulphuric acid, and pouring the mixture on to ice. *Aromatic amines* (*e.g.* p-$Cl{\cdot}C_6H_4{\cdot}NH_2$) give coloured oxidation products with persulphates and nitroso- compounds (*e.g.* $Cl{\cdot}C_6H_4{\cdot}NO$) with Caro's acid.

Thionic acids (*v.* Chem. Soc. Trans. 1880, 608).

Sulphides.

Hydrochloric acid, in most cases evolution of hydrogen sulphide; especially on heating. *Lead nitrate* or *acetate*, black precipitate (PbS). *Silver nitrate*, black precipitate (Ag_2S), insoluble in ammonia, sodium thiosulphate, and potassium cyanide. *Sodium nitroprusside*, in alkaline solutions an intense but somewhat fugitive violet colouration.

Phosphates.

Barium chloride, white precipitate $Ba_3(PO_4)_2$, soluble in dilute acids. *Calcium chloride*, white precipitate ($Ca_3(PO_4)_2$), soluble in acetic acid. *Silver nitrate*, yellow precipitate (Ag_3PO_4), soluble in nitric acid and in ammonia. *Pyrophosphates* and *metaphosphates* give white precipitates of their silver salts with silver nitrate, but metaphosphates alone, unlike ortho- and pyro-phosphates, coagulate albumin. *Magnesium sulphate*, in presence of ammonium chloride and ammonia, white crystalline precipitate ($NH_4MgPO_4 6H_2O$), soluble in acids. *Ammonium molybdate*, in nitric acid solution, on heating, a yellow precipitate ($(NH_4)_3PO_4{\cdot}12MoO_3$) soluble in ammonia, and soluble in excess of an alkaline phosphate.

Phosphites.

Barium chloride, white precipitate ($BaHPO_3$), soluble in hydrochloric acid. *Silver nitrate*, precipitate of metallic silver, especially in presence of ammonia, and on heating. *Mercuric chloride*, white precipitate (Hg_2Cl_2), becoming grey (Hg). Heated with *nitric acid*, phosphites are converted into phosphates. Heated alone, phosphites evolve phosphine. *Copper sulphate*, pale blue precipitate.

Hypophosphites.

Heated alone, evolve phosphine. *Barium chloride*, white precipitate only in strong solution ($Ba(H_2PO_2)_2$). *Silver nitrate*, metallic silver precipitated. *Copper sulphate*, brown precipitate, cuprous hydride (Cu_2H_2).

Carbonates.

Hydrochloric acid, effervescence, with evolution of carbonic anhydride, which turns lime water turbid. *Barium chloride*, white precipitate ($BaCO_3$), soluble in acids with effervescence. *Mercuric chloride*, red precipitate (basic carbonate); bicarbonates give only a yellowish opalescence. *Calcium sulphate*, white precipitate, immediately with carbonate, but only after standing with bicarbonate (Leys, J. Pharm. Chim. 1897, (vi.) 6, 441).

Borates.

Barium chloride, white precipitate in not too dilute solutions, soluble in acids. *Silver nitrate*, in strong solution, white precipitate ($AgBO_2$) in dilute solution, dark-grey deposit (Ag_2O).

Mix the solid substance with concentrated sulphuric acid in a small crucible, add alcohol, and ignite; the alcohol flame is green, especially at the edges. Mix the solid substance with three parts potassium hydrogen sulphate and one part powdered fluorspar, and heat on platinum wire in the cold area of the flame; a bright-green colouration (due to BF_3) is observed. *Turmeric paper*, moistened with acid solution of boric acid, becomes reddish brown on drying.

Silicates.

Solutions of silicates heated with acids, ammonium chloride, or ammonium carbonate, deposit silicic acid. Dilute solutions must be

evaporated to dryness, and on treating the residue with dilute hydrochloric acid insoluble silica is left.

Most silicates are insoluble in water; some are decomposed by acids; others are only decomposed by fusion with about four times their weight of a mixture of equal parts of sodium and potassium carbonates.

Silicofluorides.

Concentrated sulphuric acid, in leaden or platinum capsule, hydrogen fluoride and silicon fluoride are evolved. *Barium chloride*, colourless crystalline precipitate $BaSiF_6$. Silicofluorides on heating evolve silicon fluoride, leaving residues of metallic fluorides.

Oxalates.

Barium chloride or *calcium chloride*, white precipitate, insoluble in acetic acid, but soluble in hydrochloric acid.

Acidify with sulphuric acid, and add potassium permanganate; the colour of the latter is rapidly and completely discharged.

Heat the solid substance with concentrated sulphuric acid; carbonic anhydride and carbonic oxide are evolved. The latter burns with a blue flame.

Fluorides.

Barium chloride, white precipitate (BaF_2), soluble in hydrochloric acid. *Silver nitrate*, no precipitate with soluble fluorides. *Concentrated sulphuric acid*, especially when heated, produces hydrogen fluoride, which attacks glass. The substance and acid are placed in a small leaden or platinum crucible, which is covered with a watch-glass protected by a thin coating of wax, part of which has been scratched away so as to expose the glass.

Chlorides.

Silver nitrate, a white precipitate (AgCl), insoluble in nitric acid, soluble in ammonia; darkens when exposed to light. *Manganese dioxide* and *sulphuric acid*, evolution of chlorine on heating. *Potassium dichromate* and *strong sulphuric acid*, evolution of chromyl chloride on heating. This forms with ammonia a yellow solution of ammonium chromate.

Bromides.

Silver nitrate, yellowish white precipitate (AgBr), insoluble in nitric acid; moderately soluble in ammonia; readily soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid*, orange vapours of bromine, which turn starch paste orange. *Chlorine water* liberates bromine, which dissolves in ether or carbon bisulphite, forming an orange-brown solution. Bromides heated with *potassium dichromate* and *strong sulphuric acid* yield bromine, which forms a colourless solution with ammonia.

Iodides.

Silver nitrate, yellow precipitate (AgI), insoluble in nitric acid or ammonia; soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid* yield violet vapours of iodine, which colour starch paste blue. *Chlorine water*, *bromine water*, or *potassium dichromate in presence of hydrochloric acid*, liberates iodine, which turns starch paste an intense blue. The colour disappears on heating, and reappears on cooling. The liberated iodine may be agitated with carbon bisulphide or chloroform, when it yields a violet solution. *Nitrogen oxides in sulphuric acid* likewise liberate iodine, but do not liberate bromine unless added in large excess.

Cyanides.

Silver nitrate, white precipitate (AgCN), insoluble in nitric acid, but soluble in ammonia, sodium thiosulphate, or excess of the alkaline cyanide.

Add ferric chloride and ferrous sulphate; make alkaline with caustic potash or soda, and then acidify with hydrochloric acid. A dark-blue precipitate of Prussian blue is formed.

Evaporate the solution with an excess of yellow ammonium sulphide to complete dryness on a water-bath; dissolve in very dilute hydrochloric acid, and add ferric chloride; a blood-red colouration is produced.

Most cyanides evolve hydrocyanic acid, recognisable by the smell, when treated with hydrochloric or sulphuric acid.

Mercuric cyanide cannot be recognised by these tests. It yields cyanogen when heated in a closed tube, and is decomposed when heated with strong sulphuric acid.

Ferrocyanides.

Silver nitrate, white precipitate (Ag_4FeCy_6), insoluble in nitric acid and sparingly soluble in ammonia; soluble in potassium cyanide. *Ferric chloride*, dark-blue precipitate ($Fe_4(FeCy_6)_3$). *Ferrous sulphate*, white precipitate, rapidly becoming blue. *Copper sulphate*, chocolate-brown precipitate (Cu_2FeCy_6), or in very dilute solution a brown colouration.

Ferricyanides.

Silver nitrate, orange precipitate (Ag_3FeCy_6), soluble in ammonia; insoluble in nitric acid. *Ferrous sulphate*, dark-blue precipitate ($Fe_3(FeCy_6)_2$), insoluble in dilute acids; decomposed by alkalis. *Ferric chloride*, a greenish-brown colouration.

Thiocyanates.

Silver nitrate, white precipitate (AgCNS), soluble in ammonia; insoluble in nitric acid. *Ferric chloride*, blood-red colouration, not affected by boiling nor by hydrochloric acid; decolourised by mercuric chloride. *Copper sulphate*, a black precipitate changing to white ($Cu_2(CNS)_2$) on standing or addition of a reducing agent. *Moderately strong sulphuric acid* evolves carbon oxysulphide, which burns to carbon dioxide and sulphur dioxide. *Cobalt chloride* and the solution shaken up with ether and amyl alcohol, azure-blue colouration ($K_2Co(CNS)_4$).

Cyanates.

Cobalt chloride, in aqueous alcoholic solution, blue soluble double salt ($K_2Co(CNO)_4$), decomposed by excess of water.

Nitrates.

Sulphuric acid evolves nitric acid on heating; if metallic copper is added, red-brown nitrogen oxides are given off.

The neutral solution is mixed with ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to form a layer at the bottom; a dark-brown ring is formed at the junction of the two liquids. Iodine and bromine must be removed before applying this test, and the liquid must be cold. Nitrate in presence of nitrite: destroy nitrite by boiling acetic acid solution with urea or hydrazine sulphate; then add potassium iodide, starch, and a fragment of zinc; blue colouration denotes nitrate.

Nitrites.

Silver nitrate, a white precipitate in concentrated solutions.

Mix the solution with potassium iodide and starch and acidify with acetic acid; a deep-blue colouration is produced, owing to the liberation of iodine. Nitrites heated with dilute acids evolve nitrogen oxides. *Metaphenylenediamine hydrochloride*, Bismarck brown colouration.

A dilute solution of *α-napthylamine* and *sulphanilic acid* acidified with acetic acid; a red colouration of azo- compound (*cf.* Zeitsch. angew. Chem. 1900, 235).

Hypochlorites.

Silver nitrate, a white precipitate of silver chloride. *Lead nitrate*, a white precipitate becoming orange-red, finally brown. *Manganous salts*, a brown precipitate (MnO_2, xH_2O). *Indigo solution*, decolourised even in an alkaline solution.

Chlorates.

Warm a small quantity of the solid with concentrated sulphuric acid; a yellow explosive gas is produced with detonations.

Acidify the solution with sulphuric acid, add indigo solution, and then sulphurous acid or a sulphite drop by drop; the colour of the indigo is discharged.

Perchlorates.

Concentrated sulphuric acid, no explosive gas. *Titanous sulphate*, perchlorates reduced to chlorides.

Bromates.

Silver nitrate, white precipitate, $AgBrO_3$, decomposed by hot hydrochloric acid with evolution of bromine. *Barium chloride*, white precipitate, $Ba(BrO_3)_2$. *Sulphurous acid*, bromine liberated.

Iodates.

Silver nitrate, white curdy precipitate ($AgIO_3$), soluble in ammonia; reduced to yellow silver iodide by sulphurous acid. *Barium chloride*, white precipitate ($Ba(IO_3)_2$). *Sulphurous acid*, iodine liberated.

Periodates.

Silver nitrate, yellowish-white, red, or brown precipitate depending on the acidity of the periodate solution. *Barium chloride*, white precipitate. *Manganous sulphate*, red precipitate Mn_2HIO_6, turning brown. *Reducing agents* (H_2SO_3, $Ti_2(SO_4)_3$, Zn, etc.) convert periodates readily into iodides. *Mercuric nitrate*, orange-red precipitate $5HgO,I_2O_7$, different from iodates, which give white $Hg(IO_3)_2$.

Tartrates.

Calcium chloride, in excess, a white precipitate ($CaC_4H_4O_6$), soluble in acids and in potash solution. Complete precipitation requires time, and is promoted by vigorous agitation. *Potassium acetate*, in presence of free acetic acid, a white crystalline precipitate ($KHC_4H_4O_6$), forming slowly in dilute solutions. *Silver nitrate*, a white precipitate, soluble in nitric acid or ammonia. If the washed precipitate is dissolved in the least possible quantity of dilute ammonia, and the solution heated, the test-tube is coated with a mirror of metallic silver. *Ferrous sulphate*, followed by few drops of hydrogen peroxide and excess of caustic soda, bluish-violet colouration.

Citrates.

Calcium chloride, or *lime water*, in excess in neutral solution, a white precipitate ($Ca_3(C_6H_5O_7)_2$) only on boiling. *Potassium salts*, no precipitate. *Cadmium chloride*, gelatinous white precipitate ($Cd(C_6H_5O_7)_2$), insoluble in hot water; soluble in acetic acid (diff. from tartrates). *Mercuric sulphate* (5 p.c.), following by potassium permanganate, white turbidity, mercuric acetonedicarboxylate (halogens should be absent) (Denigès).

Malates.

Calcium chloride, no precipitate even on boiling, except in strong solutions; precipitate in dilute solutions on adding alcohol. *Lime water*, no precipitate even on boiling. *Silver nitrate*, white precipitate ($Ag_2C_4H_4O_5$), which becomes grey on boiling. *Lead acetate*, white precipitate ($PbC_4H_4O_5$), which when washed melts in boiling water.

Succinates.

Barium chloride, or *calcium chloride*, no precipitate except after addition of alcohol. *Ferric chloride*, reddish-brown precipitate ($Fe_2(C_4H_4O_4)_3$), soluble in acids; decomposed by ammonia.

Benzoates.

Hydrochloric acid, white crystalline precipitate of benzoic acid, slightly soluble in water. *Ferric chloride*, a buff precipitate ($Fe_3(C_7H_5O_2)_6$), soluble in hydrochloric acid with liberation of benzoic acid; decomposed by ammonia. *Concentrated sulphuric* acid and *alcohol* on heating produce ethyl benzoate, distinctive odour. *Soda lime*: benzoates heated with this reagent are decomposed, evolving benzene.

Salicylates.

Ferric chloride, intense purple colour; not affected by glycerol; interfered with by alkalis, dilute mineral acids, tartaric, citric, and oxalic acids, and certain other substances such as borax, sodium phosphate, ammonium and sodium acetates. *Silver nitrate*, white precipitate in neutral solutions. *Bromine water*, white precipitate, which with sodium amalgam yields phenol. *Concentrated sulphuric acid* and *methyl alcohol* on heating give methyl salicylate ('oil of winter-green'). *Diazotised aniline* or *sulphanilic acid* gives an orange azo- compound.

Acetates.

Ferric chloride, a dark-red colouration, discharged on boiling, with precipitation of a basic ferric acetate. Also discharged by hydrochloric acid. Heated with *strong sulphuric acid*, acetic acid is evolved. If alcohol is added, ethyl acetate is formed and is recognised by the smell.

Formates.

Silver nitrate, a white precipitate in concentrated solutions; the solution or precipitate rapidly becomes black (Ag), especially on heating. *Ferric chloride*, a red colour, discharged on boiling, with precipitation of basic ferric formate; also discharged by hydrochloric acid.

A solid formate mixed with concentrated sulphuric acid gives off carbonic oxide even in the cold, but no carbonic anhydride.

Gallic acid.

Ferric chloride, in neutral solutions, a bluish-black precipitate or colouration. *Gelatin* or *albumin*, no precipitate. *Potassium cyanide*, red colouration, which disappears on standing, but reappears on agitation in presence of air. *Caustic soda*, green colouration gradually

darkening, and with excess becoming brownish-red. *Lime water*, bluish-grey precipitate.

Tannic acid.

Ferric chloride, bluish-green or bluish-black precipitate or colouration. *Gelatin* or *albumin*, yellowish-white precipitate. *Potassium cyanide*, no colouration. *Caustic soda*, reddish-brown colouration gradually darkening. *Lime water*, grey precipitate.

Phenol.

Ferric chloride, violet colouration, destroyed by acids. *Bromine water*, white precipitate (tribromophenol and tribromophenol bromide). *Concentrated sulphuric acid* and a fragment of *sodium nitrite*, on gently warming, greenish blue solution, turned red when poured into water, and changed again to blue by caustic alkali.

Pyrogallol.

Silver nitrate or *Fehling's solution*, readily reduced. *Caustic alkalis*, brown solutions, rapidly darkening owing to absorption of oxygen. *Formaldehyde* and *strong hydrochloric acid*, white precipitate becoming red, and finally purple.

Uric acid.

Alkali urates reduce *silver nitrate*, and when heated with solid caustic soda, ammonia is evolved, and an alkali cyanide is produced. *Nitric acid*: evaporate solution to dryness on water-bath, reddish colouration, rendered violet by ammonia, and turned blue by caustic soda (Murexide test).

Quantitative Analysis.

Gravimetric Methods.

A few metals are separated and weighed in the metallic condition, but the majority of metallic and acidic radicles are weighed in the form of one or other of their compounds. In order that a compound may be available for the determination of one of its constituents, it should be of perfectly definite composition and not highly hygroscopic or otherwise liable to alter; it must be insoluble in the liquid in which it is formed, and insoluble in an excess of the reagent; it must be easily freed from impurities, and capable of being brought into the proper condition for weighing without tedious and complicated operations. It is also desirable that the compound should contain only a small proportion of the constituent to be estimated, since the effect of the unavoidable error of experiment is thus minimised. An estimation of chlorine in the form of silver chloride is more accurate than an estimation of silver in the same way, since only one-fourth of the error of experiment represents chlorine, whilst three-fourths represent silver.

A description will first be given of a few typical gravimetric methods; then an alphabetical list of metals and acid radicles, with a summary of methods available in each case; followed by a series of methods of separation of general applicability. Special methods for the analysis of technical products will be found in the articles dealing with these materials.

General Methods of Estimation.

I. *As Sulphides.*

(α) *With previous precipitation by hydrogen sulphide.* The solution should be moderately dilute and distinctly acidified with HCl, but any large quantity of this acid must be avoided. Nitric acid and nitrates, which should be absent as far as possible, may be removed by repeated evaporation with strong hydrochloric acid, but this treatment is not admissible if the metals present form volatile chlorides; if present, a much higher degree of dilution is necessary. In most cases precipitation is accelerated and the precipitate rendered more granular by keeping the liquid warm. A current of washed hydrogen sulphide is passed through the solution until it is thoroughly saturated, and the flask is closed and left in a warm place until the precipitate has settled. Molybdenum and the metals of the platinum group are only completely precipitated after prolonged treatment with the gas. The precipitate is protected from air as far as possible during filtration, and the liquid used for washing should contain hydrogen sulphide in order to prevent oxidation.

When arsenic is present, the liquid should be heated with pure sulphurous acid to reduce arsenic acid, and the excess of sulphurous acid expelled before treatment with hydrogen sulphide. In presence of antimony, tartaric acid should be added to prevent co-precipitation of basic antimony chloride.

When copper is precipitated as sulphide in presence of zinc, the copper sulphide should be washed once or twice with dilute hydrochloric acid of sp.gr. 1·05 containing hydrogen sulphide, and then with water also containing the gas.

(β) *With previous precipitation by ammonium sulphide.* Add to the warm solution a considerable quantity of ammonium chloride, which is found to promote precipitation and render the precipitate more granular, then ammonia to alkaline reaction, and a slight excess of ammonium sulphide. Close the flask and allow to stand in a warm place until the precipitate has settled. Protect from air as far as possible during filtration, and wash with water containing ammonium chloride and a little ammonium sulphide or hydrogen sulphide.

The precipitated sulphide is treated in one of two ways: it is collected on a weighed filter, dried at a definite temperature and weighed; or heated with sulphur in a current of hydrogen, and then weighed.

In the first case it is essential to ensure the absence of co-precipitated sulphur, and for this purpose the dried precipitate is treated with pure carbon bisulphide and again dried, or, in the case of cadmium, mercury, or bismuth, the moist precipitate is treated with a warm concentrated solution of sodium sulphite, again washed, and dried.

When the sulphide is stable at a moderately high temperature and is not reduced by hydrogen, Rose's method is employed. The dry precipitate is separated from the filter, which is then burnt, and the precipitate and filter ash are introduced into a porcelain crucible and mixed with pure finely powdered sulphur. The crucible is provided with a perforated lid, through which passes a porcelain tube connected with a hydrogen apparatus. A current of purified and dried hydrogen is passed into the crucible, which is gradually heated to full redness until excess of sulphur is expelled, allowed to cool in a current of hydrogen, and weighed.

Non-volatile sulphides may be collected in a wide Soxhlet tube and dried *in situ* over a ring burner at 300°, while a current of pure dry

carbon dioxide is conducted through the tube. This treatment removes both moisture and co-precipitated sulphur (Cahen and Morgan, Analyst, 1909, 34, 3).

II. *As Oxide.*

(*a*) *With previous precipitation as hydroxide.* The solution is mixed with ammonium chloride, heated to boiling, and ammonia added in slight excess. A large excess of ammonia will partially redissolve some of the precipitate, and must be expelled by boiling. The precipitate is washed with hot water.

If ammonia is inadmissible, pure caustic potash or soda is used as the precipitant. Excess of alkali must be avoided, and the precipitate must be very thoroughly washed, since small quantities of alkali are somewhat firmly retained.

In both cases it is better to precipitate in a porcelain or platinum vessel than in glass.

Non-volatile carbon compounds, such as sugar, glycerol, alkaline, tartrates, and citrates, &c., more or less completely prevent precipitation of hydroxides by ammonia or caustic potash, or soda, and hence must first be removed by calcination. Moderately strong nitric acid attacks filter paper, forming soluble products, which prevent the precipitation of metallic hydroxides.

(*β*) *With previous precipitation as carbonate.* The solution is nearly neutralised, heated to boiling, and mixed with a slight excess of sodium carbonate, boiling being continued until all carbon dioxide is expelled. The precipitate is washed with hot water. Ammonium carbonate can be used in some cases, and has the advantage of not introducing a fixed alkali. In these cases the precipitate should be washed with water containing a little ammonia and ammonium carbonate.

The precipitated hydroxide or carbonate is placed in a crucible (with previous separation from the filter paper if the metal is easily reducible), and is gradually heated to full redness, care being taken that no reducing gases from the flame enter the crucible. Oxides of reducible metals must be heated in a porcelain crucible, but in other cases a platinum crucible may be used with advantage. If carbonates (or oxalates) are being converted into oxides, it is important to secure a circulation of air in order to remove carbon monoxide and carbon dioxide as fast as they are given off, and thus accelerate decomposition. This is done by inclining the crucible and placing the lid across the mouth in a slanting position.

III. *As reduced Metals.*

(*a*) In some cases the metal is precipitated as oxide, which is then dried and heated in hydrogen as in Rose's method for sulphides, the reduced metal being cooled in hydrogen and weighed. This method is especially valuable when, as in the case of cobalt, the oxide obstinately retains small quantities of alkali, which, however, can readily be removed from the reduced metal by washing with water.

(*β*) The other method is to mix the oxide, carbonate, &c., with five or six times its weight of ordinary potassium cyanide, and heat in a capacious porcelain crucible, at first cautiously and afterwards to complete fusion. When reduction is complete, the crucible is allowed to cool, and is tapped occasionally to promote the collection of the reduced metal in a single button. The cyanide is removed by treatment with water, the metal washed, dried, and weighed. Care should be taken that the metallic button does not contain small fragments of porcelain resulting from the corrosion of the crucible.

IV. *As Sulphate.*

Barium, strontium, and lead are precipitated from solutions in the ordinary way, but other metals are converted into sulphate by treatment with the strong acid, the method being only available when a single metal is present in combination with a volatile acid. The highly concentrated solution, or better, the solid substance, is mixed cautiously with concentrated sulphuric acid in a platinum crucible and then gently heated to expel excess of acid, the crucible being inclined and the lid placed in a slanting position across its mouth. A large excess of acid should be avoided, and care must be taken that the temperature is sufficient to expel the excess of free acid but not sufficient to decompose the sulphate. Sulphates of the alkalis and alkaline earths may be heated to redness. Bismuth sulphate and zinc sulphate decompose if heated above 400°; magnesium sulphate is not decomposed at 450°, nor barium or lead sulphate at 500° (G. H. Bailey). A temperature of about 350° is required to expel the last traces of free sulphuric acid. With lead or bismuth sulphate a porcelain vessel must be used.

Gravimetric Determination of Metals and Acid Radicles.

Details of operations will be found under *General Methods of Estimation* (*v.* p. 179), and electrolytic and volumetric methods will be indicated under appropriate headings (*v.* p. 206).

Aluminium.

(*a*) As *oxide*, with previous precipitation with ammonium sulphide, ammonium carbonate, or as basic acetate (*v. Methods of separation*). The aluminium hydroxide is maintained in its insoluble hydrogel form by washing with dilute aqueous ammonium nitrate. The hydroxide may also be precipitated in a form suitable for filtration by boiling the solution of the aluminium salt with potassium iodide and potassium iodate (Stock, Ber. 1900, 33, 548; Compt. rend. 1900, 130, 175).

(*b*) As *phosphate.* The solution is nearly neutralised, mixed with sodium acetate and a small quantity of acetic acid, heated to boiling, sodium phosphate added in excess, and the precipitate washed with hot water, heated, and weighed as aluminium phosphate ($AlPO_4$).

Ammonium.

(*a*) As *platinichloride* $(NH_4)_2PtCl_6$ (*v. Potassium*). The platinic chloride solution should be added before the liquid is heated, and evaporation should not quite be carried to complete dryness.

(*b*) By distillation (*v.* Acidimetry).

Antimony.

(*a*) As *sulphide* Sb_2S_3 (*v.* p. 179). The precipitate is collected (i.) in a weighed Soxhlet tube on an asbestos mat, and dried at 280°–300° in a current of carbon dioxide (Analyst, 1909, 34, 3); or (ii.) in a Gooch crucible and dried in an air-oven in an atmosphere of carbon dioxide. An aliquot part is then placed in a porcelain boat, and heated in a glass tube in a current of dry carbonic anhydride until it becomes black, and

all admixed sulphur is expelled. The loss of weight is calculated to the whole quantity and deducted from the weight at 100°.

(*b*) As *oxide* Sb_2O_4, with previous precipitation as sulphide. The sulphide is placed in a porcelain crucible and treated with fuming nitric acid boiling at 86° until completely oxidised, the excess of acid expelled, and the residue heated with partial exposure to air until the weight is constant. The sulphide may also be mixed with 30 to 50 times its weight of precipitated mercuric oxide and heated cautiously until of constant weight. A deep capacious crucible with a lid having a side tube for the exit of vapours has been devised for this and similar estimations.

Arsenic.

(*a*) As *trisulphide* As_2S_3 (*v.* p. 179), which is dried at 100°. The dry precipitate should volatilise completely when heated.

(*b*) As *pentasulphide* As_2S_5. The arsenic is oxidised to arsenic acid by chlorine in alkaline solution, and the precipitation then effected in warm acid solution after decomposing all the chlorate (Brauner and Tomiček, Monatsh. 1887, 8, 642; and Neher, Zeitsch. anal. Chem. 1893, 32, 45).

(*c*) Arsenic acid is estimated as *magnesium pyroarsenate* $Mg_2As_2O_7$, in the same way as phosphoric acid (*which see*). The filter paper is moistened with a solution of ammonium nitrate and dried before burning, in order to prevent reduction (*v.* Ducru, Compt. rend. 1900, 131, 886; *cf. also* Friedheim and Michaelis, Zeitsch. anal. Chem. 1895, 34, 505).

Barium.

(*a*) As *sulphate* $BaSO_4$, by precipitation with sulphuric acid (*v. Sulphuric acid*).

(*b*) As *carbonate* $BaCO_3$, which may be dried at a temperature below dull redness after moistening the filter ash with ammonium carbonate (*v. General Methods of Estimation*).

(*c*) As *silicofluoride* (*v. Methods of separation*).

(*d*) As *bromide* (Thorne, Zeitsch. anal. Chem. 1905, 43, 308).

Glucinum.

As *oxide* GlO, with previous precipitation by ammonia or ammonium sulphide, but not caustic soda or potash, or ammonium carbonate.

Bismuth.

(*a*) As *oxide* Bi_2O_3, after precipitation with a slight excess of ammonium carbonate. In presence of chlorides or sulphates the precipitate will contain basic chloride or sulphate, and in this (or in any other) case the bismuth may be precipitated as sulphide, which is oxidised in the crucible by fuming nitric acid boiling at 86°, and then heated.

(*b*) As *sulphide* Bi_2S_3, which is dried at 100° and weighed at intervals of 20–30 minutes. The weight first decreases owing to loss of water, and then increases owing to oxidation; the minimum weight is taken as correct.

(*c*) As *metallic bismuth* (*v.* p. 180). Bismuth is precipitated as metal by adding to slightly acid solutions of its salts, formaldehyde and excess of caustic soda, boiling and filtering through a Gooch crucible, the precipitate being washed with alcohol and dried at 105° (Vanino and Treubert, Ber. 1898, 31, 1303).

(*d*) Other methods: *phosphate* (Stahler and Scharfenberg, Ber. 1905, 38, 3862), *double molybdate* $Bi(NH_4)(MoO_4)_2$ (Miller and Cruser, J. Amer. Chem. Soc. 1905, 27, 16).

Cadmium.

(*a*) As *sulphide* CdS, which is dried at 100°, or dissolved in hydrochloric acid, and the solution evaporated to dryness with sulphuric acid, the residue gently ignited and weighed as $CdSO_4$.

(*b*) As *oxide*, after precipitating as basic carbonate from boiling solutions by potassium (not sodium) carbonate and collecting in a Gooch crucible (Amer. J. Sci. 1906, 20, 456).

Calcium.

(*a*) As *oxide* CaO, after precipitation with ammonium carbonate or ammonium oxalate (*v.* Utz, Oest. Chem. Zeit. 1904, 7, 510). In the latter case the solution is made alkaline with ammonia, heated to boiling, and mixed with excess of ammonium oxalate. The precipitate is washed with hot water, and strongly heated until its weight is constant.

(*b*) As *sulphate* $CaSO_4$, by igniting the carbonate or oxalate with pure sulphuric acid.

Chromium (in chromic salts).

(*a*) As *oxide* Cr_2O_3, after precipitation by ammonia, or better, ammonium sulphide; or by potassium iodide and iodate (Stock and Massaciu, Ber. 1901, 34, 467).

(*b*) As *phosphate*, in the same way as aluminium.

Chromium (in chromic acid and chromates).

(*a*) As *oxide* Cr_2O_3. The solution is neutralised, heated to boiling, and mixed with excess of a neutral solution of mercurous nitrate free from nitrous acid. The precipitate is washed with hot water containing mercurous nitrate, and heated to redness in a porcelain crucible until all mercurial vapours are expelled. The mercurous chromate yields chromic oxide.

(*b*) As *chromate*, by precipitation with barium chloride in acetic acid solution.

Cobalt.

(*a*) As *metallic cobalt*, after precipitation as cobaltic hydroxide by caustic soda or potash with bromine (*v.* p. 180). The solution must be free from ammonium salts, or all ammonia must be expelled by boiling. The precipitate retains traces of alkali, and in accurate estimations the reduced metal should be washed with water, dried, and again heated in hydrogen.

(*b*) As *sulphate* $CoSO_4$, after precipitation as sulphide, which is treated with nitric acid and then with sulphuric acid (*v.* p. 180). If the heated sulphate is at all black, it must be treated again with sulphuric acid.

Copper.

(*a*) As *cuprous sulphide* Cu_2S, using Rose's method, with previous precipitation as cupric sulphide by hydrogen sulphide or sodium thiosulphate (Chem. Zeit. 1895, 19, 1591).

(*b*) As *oxide*, after precipitation by caustic potash or soda in absence of ammonium salts.

(*c*) As *cuprous thiocyanate* CuCNS (Rivot Compt. rend. 1854, 38, 868; also Amer. J. Sci. 1902, 13, 20 and 138). The warm solution, which must contain no free nitric acid, is slightly acidified with hydrochloric acid, and mixed gradually with an excess of a moderately strong solution of equal parts of ammonium or potassium thiocyanate and ammonium hydrogen sulphite. When cold, the precipitate is collected in a weighed Gooch crucible, washed with cold water and 20 p.c. alcohol, and dried at 110°–120°.

The precipitate may also be converted into cuprous sulphide by Rose's method. Cuprous thiocyanate is not quite insoluble, especially in presence of much free acid.

Gold.

As *metallic gold*. Nitric acid is removed by evaporation with hydrochloric acid. The solution is acidified with hydrochloric acid, mixed with a large excess of ferrous sulphate solution, and heated gently for a few hours; or it is acidified with sulphuric acid, mixed with oxalic acid, and allowed to stand in a warm place for several hours. Formaldehyde and hydrogen peroxide in alkaline solution can be used as precipitants (Ber. 1899, 32, 1968). Nitrous acid is also suggested (Jameson, J. Amer. Chem. Soc. 1905, 27, 1444). The precipitate is collected on a weighed filter, washed and dried.

Iron.

(*a*) As *ferric oxide* Fe_2O_3, after precipitation by ammonia, caustic potash or soda, potassium iodide and iodate (*v. Chromium*), or as basic carbonate, basic acetate or formate. The oxide is heated to redness until its weight is constant; if heated at a higher temperature, it is partially converted into ferroso-ferric oxide Fe_3O_4.

(*b*) Ferrous and ferric salts can be separated and estimated gravimetrically by means of barium carbonate and ammonium chloride, when the ferric salt is decomposed, precipitating ferric hydroxide, and the ferrous salt remains in solution.

Lead.

(*a*) As *sulphate* $PbSO_4$. The solution, which should not be dilute, is mixed with dilute sulphuric acid and twice its volume of alcohol, and allowed to stand, and the precipitate washed with alcohol. If the addition of alcohol is inadmissible, the solution is evaporated with a large excess of dilute sulphuric acid, till fumes are evolved. The residue is taken up with cold water and quickly filtered on a Gooch crucible; and the precipitate is washed with dilute sulphuric acid and afterwards with alcohol to remove all free acid.

(*b*) As *sulphide* PbS, by hydrogen sulphide and Rose's method.

(*c*) As *oxide* PbO, after precipitation by ammonium carbonate, avoiding an excess of ammonium salts.

(*d*) As *metal* (*v.* p. 180).

(*e*) Other methods. As *chromate* and *iodate*.

Magnesium.

(*a*) As *pyrophosphate* $Mg_2P_2O_7$. The solution is mixed with ammonium chloride in sufficient quantity to prevent precipitation by ammonia, made strongly alkaline with ammonia, and then mixed with excess of sodium phosphate, or, better, ammonium phosphate or microcosmic salt. Care should be taken to avoid rubbing or scratching the sides of the vessel. The liquid is allowed to remain for a few hours, filtered, and the precipitate washed with a mixture of strong ammonia (1 part) and water (5 parts) until the washings give only a faint opalescence with silver nitrate after acidifying with nitric acid. The precipitation of the double phosphate is greatly accelerated and a granular non-adherent product obtained by shaking the mixed solutions in a stoppered cylinder. The precipitate is dried, *cautiously* heated in a platinum crucible until all ammonia is expelled, and then heated to redness until the weight is constant. If the precipitate is black, owing to partial reduction, it is moistened with a few drops of strong nitric acid, and again heated until perfectly white.

(*b*) As *oxide* MgO, after precipitation as hydroxide by barium hydroxide, or mercuric oxide, or as double carbonate $MgCO_3(NH_4)_2CO_3$ (Zeitsch. anorg. Chem. 1908, 58, 427), the precipitate being strongly ignited (*v.* Zeitsch. anorg. Chem. 1901, 26, 347).

(*c*) As *pyroarsenate* (*v. Pyrophosphate*, and Amer. J. Sci. 1907, 23, 293).

Manganese.

(*a*) As *sulphide* MnS, by Rose's method after precipitation by ammonium sulphide.

(*b*) As *oxide* Mn_3O_4, after precipitation by sodium carbonate, or ammonium carbonate (Tamm, Zeitsch. anal. Chem. 1872, 11, 425). The hydrated peroxide precipitated by bromine and ammonia, on prolonged ignition yields Mn_3O_4.

(*c*) As *pyrophosphate* $Mn_2P_2O_7$. Ammonium chloride and microcosmic salt are added in considerable excess to the cold manganese solution followed by a slight excess of ammonia. The mixture is then heated till the precipitate becomes silky and crystalline. After cooling for 30 minutes, the precipitate is collected on the Gooch, washed with very dilute ammonia, and ignited (Gooch and Austin, Amer. J. Sci. 1898, 6, 150).

(*d*) As *sulphate* (*v.* p. 180, Gooch and Austin, Amer. J. Sci. 1898, 5, 209).

Mercury (in mercurous compounds).

As *mercurous chloride* Hg_2Cl_2. The dilute cold solution is mixed with a solution of sodium chloride in slight excess, and the precipitate is collected on a weighed filter and dried at 100°.

Mercury (in mercuric compounds).

(*a*) As *sulphide* HgS, which is dried at 100° after precipitation by hydrogen sulphide.

(*b*) As *mercurous chloride* Hg_2Cl_2. The solution is mixed with excess of hydrochloric acid and phosphorous acid (made by allowing phosphorus to oxidise slowly in moist air), and allowed to remain in a warm place for twelve hours. The precipitate is collected on a weighed filter and dried at 100°.

Molybdenum.

(*a*) As *lead molybdate* $PbMoO_4$. The solution is heated to boiling, mixed with excess of lead acetate, and boiled for a few minutes. The precipitate is washed with hot water, dried at 100°, and heated to low redness in a porcelain crucible.

(*b*) As the *oxide* MoO_3. The solution is neutralised with nitric acid, mixed with excess of a neutral solution of mercurous nitrate, the precipitate washed with mercurous nitrate solution, dried, and heated until the weight is constant. The metal is precipitated as sulphide either in acid solution, or an ammoniacal solution is saturated with hydrogen sulphide and then acidified. The precipitate, collected in a Gooch crucible, is roasted to oxide. Molybdenite is roasted to form trioxide; this is extracted with ammonia, and the filtrate evaporated and residue ignited (Analyst, 1906, 31, 312).

Nickel.

(*a*) As *oxide* NiO, after precipitation as nickelic hydroxide ($Ni(OH)_3$) by caustic potash or soda with the addition of bromine in absence of ammonium salts; or after precipitation by

ammonium sulphide thoroughly saturated with hydrogen sulphide, the nickel sulphide being dissolved in aqua regia and the solution precipitated by caustic soda or potash.

(*b*) As *dimethylglyoximate*

$$\begin{array}{l} CH_3\cdot C:NO-Ni-NO:C\cdot CH_3 \\ \quad\quad\quad\

heated too strongly) after precipitation by ammonium carbonate.

Tellurium.

(*a*) As *tellurium*, by reducing solutions of tellurous or telluric compounds with sulphur dioxide and hydrazine hydrochloride (Lenher, J. Amer. Chem. Soc. 1908, 30, 387). Other reducing agents have been employed: sulphur dioxide and potassium iodide, hypophosphorous acid, and grape sugar in alkaline solution.

(*b*) As *dioxide* TeO_2 (*v.* Amer. J. Sci. 1909, (iv.) 28, 112).

Thallium.

(*a*) As *thallous iodide* TlI. The solution is heated with sulphurous acid to reduce all the thallium compounds to thallous salts, allowed to cool, and then mixed with excess of potassium iodide. The precipitate is washed with dilute alcohol, and dried on a weighed filter at 170° (*v.* Baubigny, Compt. rend. 1892, 113, 544).

(*b*) As *thallous platinichloride*. This salt is very insoluble, but is difficult to filter (Crookes, Select Methods, 4th ed. p. 172).

Tin.

As *oxide* SnO_2, which is obtained when tin or one of its alloys is treated with nitric acid. The solution is boiled for ten minutes to ensure complete precipitation, and the precipitate is digested for an hour with dilute nitric acid (1 : 6) at 100° to remove other metals, washed with hot water, and ignited.

In other cases the tin is precipitated as hydrated oxide. If the solution contains stannous salts, the latter are oxidised by chlorine or by hydrochloric acid and potassium chlorate, ammonia added until a slight precipitate forms, and hydrochloric acid until the precipitate just redissolves. The solution is then mixed with a moderately large quantity of a strong solution of ammonium nitrate or sodium sulphate, and boiled for some time. The precipitate is washed with hot water by decantation and on the filter, dried, and heated. To ascertain if precipitation is complete, a small quantity of the filtrate is added to a hot solution of ammonium nitrate or sodium sulphate.

If the tin has been precipitated as stannic sulphide, the latter is washed with a solution of sodium chloride, and finally with a solution of ammonium acetate, dried, and roasted in a porcelain crucible until the weight is constant. Decomposition is facilitated by adding a small quantity of ammonium carbonate.

In all cases the filter is burnt separately and the ash dropped into the crucible.

Titanium.

As *dioxide* TiO_2, after precipitation by ammonia. Usually the substance is dissolved in sulphuric acid, or is fused with potassium hydrogen sulphate and dissolved in water. The solution is diluted largely and boiled for some time, when all titanium is precipitated as hydrated oxide, which is rendered anhydrous by ignition. The solution should contain 0·5 p.c. of free sulphuric acid; if less, the precipitate is impure, if more, precipitation is incomplete (Lévy). In presence of iron the results are always somewhat too high.

Baskerville recommends fusing titaniferous iron ores with potassium hydrogen sulphate containing some sodium fluoride. The product is boiled with water containing nitric acid and then neutralised with ammonia. The precipitate is dissolved in dilute hydrochloric acid, avoiding any excess. The liquid is then saturated with sulphur dioxide and boiled, the precipitate being collected, ignited, and weighed as TiO_2 (J. Soc. Chem. Ind. 1900, 19, 419; also J. Amer. Chem. Soc. 1903, 25, 1073; and 1910, 32, 957).

Tungsten.

As *tungstic anhydride* WO_3. The solution containing the tungsten as an alkaline tungstate is neutralised with nitric acid and precipitated with a neutral solution of mercurous nitrate. The precipitate is washed with a solution of mercurous nitrate, dried, and heated in a porcelain crucible, when tungstic anhydride is left.

Fused lead tungstate, when boiled with strong hydrochloric acid, gives a precipitate of tungstic acid (Brearley, Chem. News, 1899, 79, 64).

Uranium.

(*a*) As the *oxide* U_3O_8. The solution, oxidised if necessary by nitric acid, is heated to boiling and mixed with a *slight* excess of ammonia. The precipitate of acid ammonium uranate is washed with ammonium chloride solution, dried, and strongly heated.

(*b*) As the *pyrophosphate* $(UO_2)_2P_2O_7$, obtained by precipitating uranyl ammonium phosphate $(UO_2)(NH_4)PO_4$ with ammonium phosphate in the presence of ammonium acetate and igniting the precipitate at low redness. For the application of this process to uranium minerals, see Low's Technical Methods of Ore Analysis, 3rd ed. p. 223; and J. Amer. Chem. Soc. 1901, 23, 685.

Vanadium.

(*a*) As *barium pyrovanadate* $2BaO \cdot V_2O_5$. The solution is neutralised with ammonia, heated to boiling, mixed with excess of barium chloride, agitated, and cooled quickly out of contact with air. The precipitate is washed and heated.

(*b*) As *manganese pyrovanadate* $2MnO \cdot V_2O_5$. The solution is mixed with a slight excess of ammonium chloride and ammonia, manganese chloride or sulphate mixed with ammonium chloride is added in excess, and the liquid is boiled two or three minutes and allowed to cool out of contact with the air. The precipitate, which should be brownish yellow and free from oxidation products, is washed with cold water and heated.

(*c*) As *pentoxide* V_2O_5, obtained (i.) by precipitating barium or lead vanadate, decomposing with sulphuric acid, filtering, evaporating the filtrate, and igniting; (ii.) by precipitating and igniting mercury vanadate; (iii.) by precipitating ammonium vanadate by ammonium chloride and igniting the precipitate.

For other methods of estimating and separating vanadium, *v.* A. Carnot, Compt. rend. 104, 1803 and 1850; Chem. Soc. Abstr. 1887, 896; Chem. Zeit. 1905, 29, 392; Amer. J. Sci. 1910, 30, 220.

Zinc.

(*a*) As *oxide* ZnO, with previous precipitation by sodium carbonate in absence of ammonium salts.

(*b*) As *sulphide* ZnS, by Rose's method after precipitating with ammonium sulphide.

The filtration of the zinc sulphide may be promoted by precipitating in the presence of ammonium acetate or thiocyanate, and washing with a 5 p.c. solution of either of these salts. If mercuric chloride is added to the solution, the mixed precipitate of mercuric and zinc

sulphides filters much better than the latter alone; the former is expelled on ignition.

Acid Radicles.

Carbonic acid.

The estimation of carbon in carbonates may be made by a loss in weight method. The carbonate is weighed into an apparatus fitted with a stoppered dropping funnel containing acid to decompose the carbonate, and an exit tube containing strong sulphuric acid to dry the escaping gas. The apparatus is weighed with the acids, &c., after the carbonate has been introduced. The acid is then allowed to drop on the carbonate until the decomposition is complete, and the liquid boiled to expel dissolved carbon dioxide. The apparatus is again weighed and the loss of weight gives the amount of carbon dioxide. The apparatus is figured in most treatises on quantitative analysis. More accurate results are obtained by weighing the carbon dioxide directly by absorbing it in weighed tubes containing soda lime or in bulbs containing aqueous caustic potash. For a complete form of apparatus for this estimation, see Thorpe's Quantitative Analysis, 9th ed. p. 86, and Clowes and Coleman's Analysis, 8th ed. p. 104.

When carbonates and sulphides occur together, the gases evolved on treatment with acid are passed into a solution of copper acetate acidified with acetic acid and heated to boiling. Hydrogen sulphide is absorbed, with formation of copper sulphide, and carbon dioxide passes on.

For the estimation of carbon dioxide in the presence of nitrites, sulphides, and sulphites, see Marle, Chem. Soc. Trans. 1909, 1491; and Wolkowitz, Zeitsch. angew. Chem. 1894, 165.

Chloric acid.

Any chlorine present as chloride is determined, the chlorate reduced by a zinc-copper couple, and the chlorine again determined. The difference is the amount of chlorine existing as chlorate (Thorpe, Chem. Soc. Trans. 1873, 541). Thin granulated zinc is washed with caustic soda solution, then with dilute sulphuric acid, which is allowed to act for a short time, and finally with water. It is then covered with about 100 c.c. of a 3 p.c. solution of copper sulphate heated to 40°–50°. When most of the copper has been deposited, the liquid is carefully poured off, and treatment repeated with a fresh quantity of solution. The zinc-copper couple is now very carefully washed with distilled water by decantation, not more than 0·5 gram of potassium chlorate, or the equivalent quantity of any other chlorate, is weighed out into the beaker and dissolved in about 25 c.c. of warm water, which should just cover the couple. The liquid is heated gently for half an hour, then boiled for half an hour, dilute sulphuric acid added drop by drop until the white precipitate of zinc hydroxide and oxychloride just dissolves, filtered, the filtrate neutralised with pure calcium carbonate, and the chlorine estimated by standard silver nitrate solution (Chem. Soc. Trans. 1888, 166).

This reduction may also be effected by Devarda's alloy (Al 45, Zn 5, Cu 50). Jannasch recommends hydroxylamine sulphate and excess of nitric acid as a suitable reducing agent for chlorates while bromates and iodates are best reduced by hydroxylamine in ammoniacal solution (Ber. 1905, 38, 1576). Formaldehyde in dilute nitric acid reduces chlorates in 30 minutes and bromates in 2½ hours; iodates are not reduced (Grützner. Arch. Pharm. 1896, 294, 634; compare Brunner and Mellet, J. pr. Chem. 1908, 77, 33).

Hydrobromic, hydrochloric, and hydriodic acids.

As silver salts (AgBr, AgCl, AgI). The solution is mixed with excess of silver nitrate, acidified with nitric acid, and heated to boiling. The precipitate is treated exactly as in the estimation of silver.

Hydrofluoric acid.

(*a*) As *calcium fluoride* CaF_2, in the case of soluble fluorides. The solution is mixed with a moderate excess of sodium carbonate, heated to boiling, and mixed with excess of calcium chloride. The precipitate is washed, dried, and heated to redness in a platinum crucible, then treated with excess of acetic acid, evaporated to dryness, and heated to expel excess of acid. The product is now heated with water, and the insoluble calcium fluoride filtered off, washed, and heated.

(*b*) Indirectly as *silicon fluoride* SiF_4. The finely powdered solid substance is placed in a deep platinum crucible and covered with three or four times its weight of pure precipitated silica, the weight of which is accurately known. Sulphuric acid is then added, and the crucible gently heated for half an hour. The temperature is raised to expel most of the sulphuric acid, the residue treated with hydrochloric acid, washed, dried, and heated. The hydrofluoric acid is calculated from the loss in weight of the silica: $4HF = SiO_2$. The amount of silica in the substance must be known, and its weight added to that of the admixed silica.

(*c*) By *distillation and weighing as calcium fluoride.* The fluoride is decomposed by concentrated sulphuric acid in a platinum apparatus; the hydrogen fluoride carried off in a current of air and carbon dioxide and absorbed in a solution of pure caustic soda contained in a platinum dish. Calcium chloride is added to this solution and the precipitate ($CaCO_3$ and CaF_2) washed, ignited, and treated with dilute acetic acid in moderate excess. After evaporation to expel this excess of acid, the residue is taken up with water and the insoluble calcium fluoride collected, washed, and ignited (Jannasch and Röttgen, Zeitsch. anorg. Chem. 1895, 9, 267). The apparatus employed is figured in Jannasch's Praktischer Leitfaden der Gewichtsanalyse, 2nd ed. 411 (compare also J. Amer. Chem. Soc. 1901, 23, 825; and Chem. News, 1905, 92, 184).

(*d*) Directly as *silicon fluoride* (Fresenius). The mineral is finely powdered and intimately mixed with ignited quartz and heated with concentrated sulphuric acid in a dry U-tube at 150°–160°. A current of dry air free from carbon dioxide is drawn through the decomposition tube and thence through a series of five U-tubes. The first of these is empty and cooled by immersion in cold water; the second contains glass-wool, or, if the substance contains chlorine, half is filled with pumice impregnated with anhydrous copper sulphate, and the other half with pure dry calcium chloride. The third and fourth tubes

are weighed and serve to absorb the silicon fluoride; the third contains pumice moistened with water, and the fourth contains soda lime and calcium chloride. The fifth tube is a guard tube containing the same reagents as the fourth. After one or two hours the decomposition of the fluoride is complete, and the gain in weight of the absorption tubes represents the amount of silicon fluoride generated. This process may be rendered volumetric (*v. Volumetric section*).

Hydrogen sulphide (sulphides).

Insoluble sulphides are decomposed by hydrochloric acid in a flask similar to that used in the gravimetric estimation of carbonic acid, and the gas evolved is led into two or three bulb U-tubes containing a solution of bromine in dilute hydrochloric acid, which converts the hydrogen sulphide into sulphuric acid. When decomposition is complete, the liquid in the flask is boiled, and the last traces of the gas are drawn through the bulbs by means of an aspirator. The contents of the bulb tubes are transferred to a beaker, heated to expel bromine, and the sulphuric acid precipitated by barium chloride.

Sulphides which are not decomposed by hydrochloric acid may be oxidised with aqua regia, hydrochloric acid and bromine, or hydrochloric acid and potassium chlorate, the sulphuric acid formed being weighed as barium sulphate.

Nitric acid.

(*a*) Indirectly, as ammonia, by means of the zinc-copper couple (Thorpe). A zinc-copper couple (*v. Chloric acid*) is made in a flask into which is weighed a quantity of the nitrate corresponding with not more than 0·5 gram of potassium nitrate, and sufficient water is added to just cover the couple. The flask is attached to a condenser, the other end of which is connected with a U-tube or flask containing hydrochloric acid, as in the estimation of ammonia. The liquid is gently heated for some time, and then distilled nearly to dryness. After cooling, a further quantity of water is added to the couple, and distillation repeated. The ammonia in the distillate is estimated as platinichloride, or is received in a measured volume of standard acid and titrated. The reduction can also be conveniently effected by the use of Devarda's alloy (*v. Chloric acid*) in alkaline solution (Analyst, 1910, 35, 307).

(*b*) *Schloesing's method.* When a solution of a nitrate is heated with an acid solution of a ferrous salt, the nitrate is decomposed, the whole of the nitrogen being evolved as nitric oxide, which is measured. The difficulty lies mainly in obtaining the nitric oxide free from air. The apparatus employed consists of a *small* distilling flask provided with a side tube which terminates under a gas-collecting tube in a mercurial trough. The neck of the flask is fitted with a cork, which carries a tube funnel provided with a stop-cock and another tube connected with a carbon-dioxide apparatus. Carbon dioxide *free from air* is passed into the apparatus until all air is expelled and the gas issuing from the exit tube is completely absorbed by caustic potash. The substance containing the nitrate, which must be in the solid condition, is dissolved in 2 or 3 c.c. of concentrated ferrous chloride solution, mixed with 1 c.c. of strong hydrochloric acid, and introduced into the flask by means of the funnel tube, care being taken that no air enters. The dish and the funnel are rinsed with very small quantities of acid, the object being to use as little liquid as possible. The contents of the flask are then rapidly boiled to dryness, the evolved gas being collected in the tube over mercury, and carbon dioxide is driven through the apparatus to expel all nitric oxide. The mixture of nitric oxide and carbon dioxide is transferred to an apparatus for gas analysis; the latter absorbed by caustic potash, and the former mixed with oxygen and absorbed by alkaline pyrogallol. Nitrites are converted into nitrates by addition of hydrogen peroxide during evaporation of the original solution (*v.* Warington, Chem. Soc. Trans. 1880, 468, and 1882, 345).

(*c*) *By standard indigo solution* (Warington, Chem. News, 35, 45, and Chem. Soc. Trans. 1879, 578).

(*d*) As 1 : 4-*diphenyl*-3 : 5-*endanilodihydrotriazole nitrate* $C_{20}H_{18}N_4,HNO_3$. A 10 p.c. solution of the base 1 : 4-diphenyl-3 : 5-endanilohydrotriazole 'Nitron,'

in 5 p.c. acetic acid produces a voluminous white precipitate in dilute nitric acid or nitrate solution. Nitrites interfere by giving a sparingly soluble salt with this base; they are removed by hydrazine sulphate. Bromides, iodides, chlorates, perchlorates, and chromates, are also precipitated by nitron, and must be removed. Organic matters do not seriously affect the method, which has been tested successfully with solutions containing 0·5 p.c. of gelatine, and 2 p.c. of dextrin (Busch, Ber. 1905, 38, 861). The method gives favourable results for nitrates in water or fertilisers (Collins, Analyst, 1907, 32, 349).

(*e*) Howard and Chick have shown that cinchonamine gives a very insoluble nitrate and can be used in estimating nitric acid and its salts (J. Soc. Chem. Ind. 1909, 28, 53).

Oxalic acid.

As *calcium oxalate.* The method is already indicated under *Calcium.*

Phosphoric acid.

As *magnesium pyrophosphate* $Mg_2P_2O_7$. The operation is conducted as in the estimation of magnesium. If magnesium sulphate is used as the precipitant, the precipitate may be contaminated with basic magnesium sulphate; it is therefore advisable to employ a solution of the chloride, which is made as follows: 85 grams of crystallised magnesium sulphate are dissolved in boiling water, acidified with 5 c.c. of hydrochloric acid, mixed with an aqueous solution of 82 grams of crystallised barium chloride, boiled, and filtered. A few drops of magnesium sulphate solution are added to be sure that there is no excess of barium, then 165 grams of pure ammonium chloride, and 260 c.c. of ammonia, and the solution diluted to 1 litre. After two or three days the solution is filtered. In many cases the phosphoric acid is first separated by ammonium molybdate (*v. Methods of separation*).

Silicic acid.

As *silica* SiO_2. Soluble silicates are acidified with hydrochloric acid and evaporated to complete dryness; moistened with strong hydro-

chloric acid, again evaporated to dryness, the residue treated with dilute acid, and the insoluble silica washed with hot water and ignited.

Insoluble silicates are very finely powdered, intimately mixed with about five times their weight of a dry mixture of sodium and potassium carbonates in equal proportions, and heated to redness in a platinum crucible for half an hour. The cooled mass is treated with water, acidified with hydrochloric acid, and evaporated as above.

(For the separation of silica when the alkalis have to be estimated, *v. Methods of separation*, Group VI.)

Sulphuric acid.

As *barium sulphate* $BaSO_4$, by precipitation with barium chloride. The chief difficulty arises from the tendency of the barium sulphate to separate in a finely divided condition and to carry down impurities, especially in presence of nitrates and potassium salts. These sources of error are avoided by taking care that the solution is somewhat dilute, is free from nitrates, and contains a moderate but not excessive quantity of free hydrochloric acid. The solution and the barium chloride solution should both be heated to boiling, and mixed *gradually, with continual agitation.* The liquid may be filtered as soon as it has become clear, and the precipitate is washed with hot water and heated to dull redness. If too little hydrochloric acid is present, the precipitate is liable to be impure; if a very large excess of the acid is present, precipitation is not quite complete (compare Allen and Johnston, J. Amer. Chem. Soc. 1910, 32, 588).

Sulphurous acid.

Indirectly as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

Thiosulphuric acid.

Indirectly as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

Water is usually estimated by difference. If a direct determination is required, the method to be adopted will depend upon circumstances. In many cases it is sufficient to heat the substance on a watch-glass, or in a crucible in a drying oven, at a definite temperature, until the weight is constant. During weighing the dried substance must be carefully protected from the air. Attention must, however, be paid to the possibility of the volatilisation of substances other than water. Many hydrated haloid salts, for example, lose part of their acid. In such cases the substance is previously mixed with a known weight of perfectly dry lead monoxide. Ammonia, ammonium salts, and volatile organic matter may also be given off. If the drying is conducted in a glass tube, the vapours may be led into standard acid and the ammonia determined by titration: the total loss, *minus* the ammonia, gives the amount of water. Some substances increase in weight in consequence of oxidation. Frequently it is desirable to collect the evolved water and weigh it directly. The substance is introduced into a glass tube (plain, or with a bulb in the middle) drawn out and bent at right angles at one end, which passes directly, without any intervening indiarubber tube, through the cork of a U-tube containing either calcium chloride or pumice moistened with strong sulphuric acid (*v.* ORGANIC ANALYSIS).

All fluosilicates, even topaz, evolve silicon fluoride on ignition, and water is estimated by mixing the mineral with lead oxide in a hard glass tube, heating the mixture in a current of dry air and passing the gases over a layer of lead oxide contained in the same tube. The water is collected and weighed in calcium chloride tubes.

METHODS OF SEPARATION.

A. *The Estimation of the Metals in their Ores and Alloys.*

In this section the metals are arranged in the order in which they occur in the qualitative groups. Both gravimetric and volumetric methods are included in this description, the latter being indicated wherever possible, owing to the greater rapidity with which the analysis can be executed.

GROUP I.

Silver is separated from all other metals by treating its ores and alloys with moderately strong nitric acid, evaporating off excess of solvent, diluting with water, and adding to the filtered solution either hydrochloric acid or sodium chloride. To remove any lead or thallous chloride which may be present, the precipitate is extracted repeatedly with warm water; it should, however, be remembered that silver chloride is not absolutely insoluble in hot water. Silver is conveniently estimated volumetrically in the above dilute nitric acid solution, after boiling off nitrous fumes, by adding ferric indicator and titrating with standard ammonium thiocyanate in accordance with Volhard's method (*see Volumetric section*). The presence of other metals having colourless salts does not interfere with this process; nickel, cobalt, and copper must not be present to any large extent, and mercury should be absent because of the insolubility of mercuric thiocyanate. When more than 60 p.c. of copper is present, the silver is precipitated with excess of alkali thiocyanate. The well-washed silver thiocyanate is decomposed by strong nitric acid, the sulphuric acid produced precipitated by barium nitrate, and the Volhard titration effected without filtering off the barium sulphate (*v.* Ber. 1905, 38, 566).

The silver in argentiferous galena is estimated by fusing the sulphide with crude potassium hydrogen tartrate (argol), and sodium carbonate in an iron crucible, and by heating the lead-silver button thus obtained in a porous bone-ash crucible ('cupel') until the lead is removed as oxide, partly by volatilisation and partly by absorption into the cupel. The residual silver is detached from the cold cupel and weighed.

Gold quartz is assayed for silver by heating the mineral with lead oxide, and a reducing flux, when the lead produced extracts both the gold and silver. This alloy is cupelled, and the silver-gold button is 'parted' by heating with strong nitric acid diluted with three parts of water; the residual gold is collected, ignited, and weighed. The silver is precipitated by hydrochloric acid from the nitric acid solution. When more than 30 p.c. of gold is present in the button before parting, this metal will retain silver. In order to prevent this retention, a known weight of silver is added to the fused button. (For further details of the separations of gold, silver, and lead in the dry way, see ASSAYING, pp. 322-327.)

Thallium, in the more stable thallous condition to which thallic salts are readily reduced, is separated from the metals of Group II. by precipitating the latter with hydrogen sulphide in acid solution. Alkali hydroxides separate it from all metals, giving insoluble hydroxides, and ammonium sulphide, which precipitates thallous sulphide, separates this metal from the alkalis and alkaline earths. Gravimetrically, thallium can be weighed as acid sulphate $TlHSO_4$, stable at 240°, and as sulphate Tl_2SO_4, stable at low red heat; it can be precipitated and weighed as iodide TlI, platinichloride Tl_2PtCl_6, and chromate Tl_2CrO_4. Volumetrically, it can be estimated by the oxidation of thallous salts by permanganate or by titrating with thiosulphate the iodine set free in accordance with the following reaction: $TlCl_3 + 3KI = TlI + 3KCl + I_2$ (Chem. Soc. Proc. 1908, 24, 75).

GROUP II.

Mercury in its ores is generally estimated by distillation with quicklime in a current of coal gas or carbon dioxide. The decomposition of the mercury compounds is facilitated by mixing copper strips with the quicklime, and the presence of this reducing agent is essential in the case of mercuric iodide. The mercury which distils over is collected under water, washed, dried, and weighed. Ores containing only small amounts of mercury are decomposed by heating

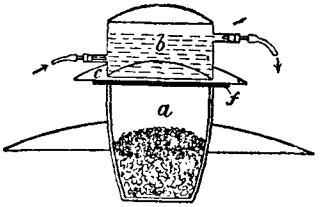


FIG. 8.

with iron filings in a porcelain crucible, *a*, having a silver lid, *f*, which is cooled by a water-jacket, *b*, laid upon it. The mercury condenses on the under surface of the silver plate, *f*, which is weighed before and after the experiment (*v.* Holloway, Analyst, 1906, 31, 66).

Mercury is separated from all other metals in the wet way by dissolving the ore or alloy in nitric acid or aqua regia, diluting considerably, precipitating the sulphides of Group II. by hydrogen sulphide, removing the arsenic-tin sub-group by means of yellow ammonium sulphide (*not* sodium sulphide or hydroxide), treating the residual sulphides with dilute nitric acid (sp.gr. 1·2–1·3), and dissolving the final residue in aqua regia and filtering if necessary from sulphur and lead sulphate. The mercury can be reprecipitated by almost neutralising the acid solution, adding in succession ammonium sulphide, caustic soda and ammonium nitrate. The caustic soda redissolves the sulphide initially formed as the soluble double sulphide $Hg(SNa)_2$, and from this the ammonium nitrate reprecipitates mercuric sulphide in a form suitable for collection. The precipitate is washed successively with water, alcohol, and carbon disulphide, dried at 110°, and weighed as HgS. (For other methods of separating mercury, see Jannasch, Zeitsch. anorg. Chem. 1896, 12, 132, and 359; and Stähler, Chem. Zeit. 1907, 31, 615.)

Lead in its ores and alloys is usually separated from other metals by dissolving the substance in hydrochloric or nitric acid, or if necessary in a mixture of the two acids, and evaporating down the solution with sulphuric acid until white fumes are evolved. The mixture is then cooled diluted with water, and the lead sulphate quickly collected. If the amount of lead is small, alcohol must be added to complete the precipitation. The lead sulphate thus obtained is freed from silica, stannic oxide, and other impurities by dissolving it in an excess of ammonium or sodium acetate.

When separated as lead sulphate, the lead can be estimated volumetrically by boiling the precipitate with ammonium carbonate and then dissolving the lead carbonate in acetic acid. The lead is thus converted into lead acetate which is titrated with standard ferrocyanide using as indicator drops of uranium acetate on a porcelain plate. The lead may also be reprecipitated as oxalate from the acetate solution by alkali oxalate, the washed lead oxalate being then suspended in dilute sulphuric acid, and titrated with standard permanganate. From the solution of the sulphate in sodium acetate the lead can be precipitated as chromate by potassium dichromate. The chromate is dissolved in dilute nitric acid, and reduced with methyl or ethyl alcohol. The solution, rendered ammoniacal, is treated with oxalic acid, when lead is precipitated and titrated as above with standard permanganate (*v.* Chem. News, 1896, 73, 18; J. Amer. Chem. Soc. 1896, 18, 737; Zeitsch. anal. Chem. 1902, 41, 653). Lead may be separated from copper by electrolysing a solution of the metals in dilute nitric acid with a weak current (0·5–1·5 amperes and 1·4 volts), when the lead is precipitated as dioxide on the anode (a platinum dish with unpolished inner surface).

Bismuth is separated from all other metals but those of Group II. by the precipitation of its sulphide by hydrogen sulphide in acid solution. The insolubility of the sulphide in ammonium sulphide separates this metal from arsenic, antimony, and tin. The further separation of bismuth from mercury, copper, and cadmium presents no particular difficulty, and is effected by taking advantage of the solubility of bismuth sulphide in nitric acid (sp.gr. 1·25), and the precipitation of bismuth oxychloride on diluting considerably an acid solution of bismuth chloride. The problem of separating bismuth from lead is, however, much more troublesome, and the following appear to be most trustworthy methods: (i.) the separation of the bismuth as basic nitrate and the solution of lead nitrate in dilute ammonium nitrate (J. pr. Chem. 1858, 74, 345); (ii.) the distillation of the mixed sulphides in a current of bromine, when bismuth bromide is volatilised, leaving behind lead bromide (Jannasch, Praktischer Leitfaden der Gewichtsanalyse, 1st ed. 155); (iii.) the precipitation of bismuth as the basic formate; a repetition of this operation gives a precipitate free from lead, which is dissolved in dilute nitric acid, the solution almost neutralised with sodium carbonate, and the bismuth then finally precipitated and weighed as phosphate $BiPO_4$ (Stähler, Chem. Zeit. 1907, 31, 615). The lead in the filtrate from the formate separation is precipitated as sulphide, converted into sulphate, and weighed as such. This method

of separation gives accurate results (Little and Cahen, Analyst, 1910, 35, 301).

Copper is separated from the metals of Groups III., IV., V., and VI., by precipitation as sulphide by hydrogen sulphide in acid solution. In alloys and ores it is generally separated from antimony and tin by rendering these insoluble by the action of moderately strong nitric acid. If, however, the sulphides of these metals and arsenic are present, they are extracted from the precipitate with alkali sulphides (not ammonium sulphide). The insoluble residue, containing the sulphides of copper, bismuth, lead, mercury, and cadmium, is treated with nitric acid (*v. Mercury* and *Bismuth*). Copper is readily separated from bismuth by means of ammonium carbonate, which precipitates basic bismuth carbonate, leaving copper in solution. The separation from cadmium may be effected by one of the following methods:—(1) Hydrogen sulphide is passed into a boiling solution of the sulphates of copper and cadmium in dilute sulphuric acid (1 : 4). The precipitated copper sulphide, which contains some cadmium, is redissolved in nitric acid, and, after expelling excess of the solvent, the precipitation is repeated. (2) The copper is precipitated as cuprous thiocyanate, leaving cadmium in solution. (3) The copper is converted into potassium cuprocyanide $K_3Cu(CN)_4$, with a considerable excess of potassium cyanide, and the cadmium precipitated with hydrogen sulphide or ammonium sulphide (compare also Browning, Amer. J. Sci. 1893, [3] 46, 280).

The following volumetric processes for copper are employed in the technical analysis of the ores of this metal. (i.) The mineral is dissolved in hydrochloric and nitric acids, and the solution boiled down with sulphuric acid to expel the volatile acids. The copper is precipitated from the boiling solution by introducing a sheet of aluminium and redissolving in nitric acid with the addition of bromine to destroy nitrous fumes. The solution is neutralised with ammonia, acidified with acetic acid, and treated with excess of potassium iodide, when the liberated iodine is titrated with standard thiosulphate (Low, J. Amer. Chem. Soc. 1902, 24, 1082). (ii.) A solution of potassium cyanide is standardised against pure copper foil by dissolving the latter in nitric acid, adding bromine, boiling to expel nitrous fumes and excess of bromine, adding ammonia till strongly alkaline, and titrating with the cyanide solution until the blue tint disappears. The copper ore is treated as in (*i.*), the copper being precipitated by aluminium, redissolved in nitric acid, and the resulting solution titrated in manner just described (*v.* Brearley, Chem. News, 1897 76, 189). (For other methods of separating and estimating copper, see also Zeitsch. anorg. Chem. 1896, ii. 268; Chem. Soc. Abstr. 1901, ii. 197; J. Amer. Chem. Soc. 1905, 27, 1224; Zeitsch. anal. Chem. 1907, 46, 128; J. Amer. Chem. Soc. 1908, 30, 760; Chem. Zeit. 1908, 33, 263; Amer. J. Sci. 1909, (iv.) 27, 448.)

(For electrolytic estimation of copper, *see* p. 250.)

Cadmium is separated from the other metals of Group II. by the methods indicated under *copper*, *lead*, &c. In the presence of zinc, Fox recommends precipitation in a solution containing trichloroacetic acid (Chem. Soc. Trans. 1907, 91, 964). Electrolytically, cadmium is deposited from a cyanide solution (0·7–1·2 amperes and 4·8–5 volts); the use of a rotating cathode accelerates the rate of deposition (compare Flora, Amer. J. Sci. 1906, 70, 268 and 392; and Avery and Dales, J. Amer. Chem. Soc. 1897, 19, 379).

Tin, *antimony*, and *arsenic* are separated from the remaining metals of Group II. by digesting the group precipitate at 80° with concentrated yellow ammonium sulphide, when the sulphides of these three metals dissolve, leaving the other sulphides insoluble. Copper sulphide is appreciably soluble in this solvent, and in the presence of copper it is preferable to use sodium or potassium sulphide, but in the presence of mercury these reagents are inadmissible, owing to formation of the soluble double sulphide $Hg(SK)_2$. In the presence of much lead a small amount of tin is retained in the insoluble residue. Arsenic rarely occurs in alloys, and in these substances antimony and tin are separated from other metals as insoluble oxy-acids (metantimonic and metastannic acids) by the use of nitric acid as solvent.

Arsenic is separated from antimony and tin by distilling the hydrochloric acid solution of the three elements with ferrous chloride; the arsenic is volatilised as arsenious chloride; this compound is collected in cold water and the arsenic precipitated as trisulphide (Fischer, Zeitsch. anal. Chem. 1881, 21, 266). Various modifications of this method have been introduced; the distillation is carried on in a current of hydrogen chloride and hydrogen sulphide, the latter serving as the reducing agent instead of ferrous chloride; the volatilised arsenious chloride is converted in the cooled receiver into the trisulphide (Piloty and Stock, Ber. 1897, 30, 1649). (For other modifications, *see* Gooch and Danner, Amer. J. Sci. 1891, [3] 42, 308; Andrews, J. Amer. Chem. Soc. 1895, 17, 869; Rohmer, Ber. 1901, 34, 33; Morgan, Chem. Soc. Trans. 1904, 85, 1001.)

The arsenic may also be separated from tin and antimony by dissolving the three sulphides in ammoniacal hydrogen peroxide, neutralising the solution with mineral acid, acidifying with tartaric acid, and precipitating the arsenic as magnesium ammonium arsenate by the addition of ammonia and magnesia mixture (*see Qualitative analysis*).

The following method of separating arsenic and antimony in their ores, leads to volumetric processes for the determination of these elements (Low, J. Amer. Chem. Soc. 1906, 28, 1715). The mineral is decomposed by heating with strong sulphuric acid (20 parts) containing potassium hydrogen sulphate (1·4 parts), and 1 part of tartaric acid. The cooled product is taken up with 350 c.c. of hot water, 10 c.c. of strong hydrochloric acid, and 3 grams of tartaric acid, and the solution saturated with hydrogen sulphide. The mixed sulphides are dissolved in aqueous potassium sulphide, and the filtrate evaporated down with 10 c.c. of strong sulphuric acid and 3 grams of potassium hydrogen sulphate until the sulphur and the greater part of the free aid are expelled. The cooled melt is dissolved in 50 c.c. of strong hydrochloric acid and 25 c.c. of water, and arsenious sulphide precipitated by hydrogen sulphide. The antimony remaining in the filtrate is precipitated as sulphide by

diluting the solution and passing in more hydrogen sulphide. The antimonious sulphide is again dissolved in potassium sulphide, the solution evaporated nearly to dryness with strong sulphuric acid and potassium hydrogen sulphate, the melt dissolved in dilute hydrochloric acid and titrated with standard permanganate.

The arsenious sulphide is dissolved in warm ammonium sulphide, and the solution heated strongly with strong sulphuric acid and potassium hydrogen sulphate until all the sulphur and nearly all the acid are expelled. The residue is boiled with water to expel sulphur dioxide, neutralised, and titrated with standard iodine solution in the presence of sodium bicarbonate.

Arsenic may also be estimated in minerals (which do not contain phosphates) by fusing the powdered ore with sodium carbonate and nitre or sodium peroxide, extracting the fused mass with water and precipitating silver arsenate from the neutralised solution. This precipitate is redissolved in nitric acid, and the amount of silver in it determined by standard thiocyanate; whence the quantity of arsenic present can be readily calculated. (For other processes for the estimation of arsenic in technically important materials, *v.* Clark, Chem. Soc. Trans. 1892, 61, 424; Friedheim, Zeitsch. anal. Chem. 1905, 44, 665; Heath, Zeitsch. anorg. Chem. 1908, 59, 87; Gooch and Phelps, Amer. J. Sci. 1906, (iv.) 22, 488; McGowan and Floris, J. Soc. Chem. Ind. 1905, 24, 265; Sanger and Black, *ibid.* 26, 1115.) (For the detection and estimation of minute quantities of arsenic, *v.* ARSENIC.)

Separation of tin and antimony. In the absence of any large amount of lead or other metal giving a sulphide insoluble in ammonium sulphide, tin and antimony can be separated from these metals by means of this reagent, but if lead is present in considerable amount the tin is never completely extracted, a portion always remaining in the insoluble residue. In this case it is preferable to separate out the tin and antimony by oxidising them to their insoluble hydrated oxides by means of nitric acid. These oxides when fused with caustic soda in a silver crucible yield sodium stannate and antimonate; the latter of these salts is practically insoluble in dilute alcohol (1 vol. alcohol, 2 vols. water), whilst the former is readily dissolved. A repetition of this process with the insoluble antimonate leads to a complete separation.

When present as sulphides, these metals are conveniently dealt with by Henz's modification of Clark's method. The sulphides are dissolved in excess of aqueous caustic potash containing potassium tartrate; the solution is gradually heated to boiling with excess of 30 p.c. hydrogen peroxide. When the oxidation of the sulphides is complete, excess of oxalic acid is added (15 grams for 1 gram of mixed metal), the liquid boiled to destroy excess of hydrogen peroxide, and hydrogen sulphide passed for some time through the hot solution. The precipitated antimony sulphide is dealt with as described under gravimetric estimations (p. 180). The filtrate is treated with sulphuric acid, concentrated to a small bulk (150 c.c.), and electrolysed at 60° with a current of 0·2–0·3 ampere, and 2·3 volts, using a rotating anode, when the deposition of the tin is complete in about one hour (Henz. Zeitsch. anorg. Chem. 1903, 37, 1; and Cahen and Morgan, Analyst, 1909, 34, 3).

In Clark's original process the filtrate from the antimony sulphide, which contains stannic tin, is mixed with yellow ammonium sulphide in excess and acidified with acetic acid. After some time the stannic sulphide is collected, washed with a solution of ammonium nitrate, and converted into stannic oxide by ignition. In accurate work the antimony sulphide is redissolved, and the oxalic acid separation repeated in order to obtain the last traces of tin (compare Carnot, Compt. rend, 1886, 103, 258). (For descriptions of other methods of estimating tin and antimony in their ores and alloys, see J. Soc. Chem. Ind. 1892, 11, 662; G. W. Thompson, J. Soc. Chem. Ind. 1896, 15, 179; T. Brown, jun., J. Amer. Chem. Soc. 1899, 21, 780; Argenot, Zeitsch. angew. Chem. 1904, 17, 1274; Lévy, Analyst, 1905, 30, 361; Panajotow, Ber. 1909, 42, 1296.)

The following process, due to Pearce, gives a rapid volumetric method for estimating tin in its ores. The mineral is fused in a nickel crucible with about 20 parts of sodium hydroxide with the addition of a little powdered charcoal; the fused mass is dissolved (excepting silica) in hydrochloric acid, and the solution reduced by the addition of iron rods or sheet nickel. The stannous chloride thus produced is titrated with standard iodine solution in presence of sufficient hydrochloric acid (1 : 4) to prevent the oxidation of any arsenic or antimony which may be present.

Gold and *platinum* are separated chiefly in the analytical subgroup containing arsenic, antimony, and tin. Fusion of the sulphides with sodium carbonate and nitre, followed by extraction with water, removes the arsenic. The residue, treated with zinc and hydrochloric acid, reduces tin and antimony to the metallic state; the former is dissolved by boiling hydrochloric acid, and the latter by nitric and tartaric acids, whilst gold and platinum are left. Treatment of the mixed metals with chlorine water removes gold, and dilute *aqua regia* then dissolves platinum, palladium, and rhodium. From this solution platinum is precipitated by ammonium chloride and alcohol, and from the filtrate, after neutralisation with sodium carbonate, palladium is precipitated as cyanide by mercuric cyanide.

The residue from the *aqua regia* treatment is roasted in the air; osmium volatilises as the tetroxide, ruthenium sublimes as the dioxide, whilst iridium is left (*v.* Leidié, Compt. rend. 1900, 131, 888; and PLATINUM METALS).

Molybdenum is precipitated as sulphide preferably from a sulphuric acid solution by treatment with hydrogen sulphide under pressure. From the sulphides of the copper-lead subgroup, it is separated by digestion with sodium sulphide under pressure, when the molybdenum passes into solution and is reprecipitated as sulphide by dilute sulphuric acid. Molybdenum sulphide is separated from the sulphides of antimony and tin by dissolving the latter in hydrochloric acid. The sulphides of arsenic and molybdenum are dissolved in hydrochloric acid and potassium chlorate, the arsenic precipitated from the filtrate after adding ammonia and magnesia mixture as magnesium ammonium

arsenate. The final filtrate is acidified, and the molybdenum reprecipitated as sulphide. Molybdenum is separated from phosphorus in a similar manner. From tungsten it is best separated by heating the mixed trioxides or their alkali salts at 250°–270° in a current of hydrogen chloride, when the molybdenum is completely volatilised as the additive compound $MoO_3,2HCl$, while the tungsten remains in the non-volatile residue (Debray, Compt. rend. 1858, 46, 1101: and Péchard, *ibid.* 1892, 114, 173).

Selenium and *tellurium* fall into the analytical sub-group containing arsenic, and after this element has been removed as magnesium ammonium arsenate (*v. Molybdenum*), the selenium and tellurium are precipitated by reducing agents such as sulphur dioxide, hydrazine, &c. (i.) Sulphur, selenium, and tellurium are separated by fusion with potassium cyanide in a stream of hydrogen. On dissolving the mass in water and passing air through the solution, the potassium telluride present is decomposed, and tellurium is precipitated. When the filtrate is acidified, the potassium selenocyanate (KCNSe) is decomposed, yielding selenium. (ii.) The mixed dioxides of selenium and *tellurium* are dissolved in aqueous caustic potash; the solution, faintly acidified with hydrochloric acid, is diluted to at least 200 c.c. with boiling water, rendered just ammoniacal and reacidified with acetic acid. After 30 minutes the tellurium dioxide is collected, washed with cold water, and gently ignited (Browning and Flint, Zeitsch. anorg. Chem. 1909, 64, 104).

Gold from all other metals: reduction of an acid solution by oxalic acid or sulphurous acid.

Selenium from the metals: reduction with sulphurous acid in hydrochloric acid solution.

Group III.—The metals of Group III*a.* are separated from those of the succeeding groups by precipitation with ammonia in presence of ammonium chloride; the metals of Group III*b.* are separated from those of the succeeding groups by means of ammonium sulphide (*v. General methods of estimation*).

Iron, aluminium, chromium, uranium, glucinum, and cerium, from zinc, manganese, nickel, cobalt. The solution, which must contain iron and uranium as ferric and uranic salts, is nearly neutralised, mixed with excess of finely divided and recently precipitated barium carbonate, and allowed to remain in a closed vessel at the ordinary temperature for some hours with occasional agitation. In presence of nickel and cobalt, ammonium chloride should be added to prevent precipitation of traces of these metals. Filter and wash with cold water. The precipitate may contain ferric, chromic, aluminium, glucinum, ceric and uranic hydroxides, mixed with barium carbonate; the filtrate contains the other metals, together with some barium. In both cases the barium can be removed by means of sulphuric acid, but as the barium sulphate carries down small amounts of the other metals, it is preferable to separate the metals of Groups III. and IV. by a double precipitation with ammonium sulphide (Treadwell).

Iron and aluminium from zinc, manganese, nickel, cobalt, uranium, and metals of the succeeding groups. The solution, which must contain iron as a ferric salt, is nearly neutralised by sodium or ammonium carbonate. In presence of iron the liquid becomes deep red, but no precipitate must be formed. Sodium, or, better, ammonium acetate, is added in sufficient but not excessive quantity, and the liquid is boiled until the precipitate becomes granular and settles rapidly. Prolonged boiling makes the precipitate slimy. The liquid is filtered whilst hot, and the precipitate is washed with hot water; if the liquid is allowed to cool the precipitate is partially redissolved. The precipitate is converted into ferric and aluminium oxides by ignition; the other metals are in the filtrate. It is advisable, and in presence of nickel essential, to redissolve the precipitate and repeat the process. This method is not available for the separation of chromium.

The same result can be obtained with ammonium formate or succinate.

Aluminium and chromium from iron, zinc, manganese, nickel, and cobalt. Mix the solution with a moderate quantity of pure normal potassium tartrate, then with pure caustic potash or soda until the precipitate redissolves, add ammonium sulphide in slight excess and allow to stand. Wash the precipitate with water containing ammonium sulphide. Aluminium and chromium are in the filtrate, the other metals in the precipitate. If iron and chromium are absent, it is sufficient to add the alkaline tartrate, excess of ammonia, ammonium chloride and ammonium sulphide.

Separation of iron and aluminium. The following methods have also been employed for this important separation. (i.) Potassium hydroxide dissolves aluminium hydroxide, but not ferric hydroxide; the former is reprecipitated from the filtrate by boiling with ammonium chloride or adding successively nitric acid and ammonia; the iron precipitate is dissolved in acid and reprecipitated by ammonia. (ii.) The two metals are precipitated with ammonia and the weight of the combined oxides determined. The mixture is then digested with strong hydrochloric acid (10 concentrated solution : 1 water) until all the iron has dissolved; the presence of free chlorine or hydriodic acid assists the solution of the ferric oxide. If alumina predominates, it may be necessary to fuse the mixed oxides with potassium pyrosulphate. The solution is saturated with hydrogen sulphide to reduce the iron to the ferrous condition; the excess of this sulphide is expelled by carbon dioxide, and the liquid titrated with standard permanganate. The proportion of aluminium is determined by difference. (iii.) Iron and aluminium may also be separated by treating the mixed chlorides with strong hydrochloric acid and ether (equal vols.); the aluminium chloride is precipitated, collected, washed with ethereal hydrochloric acid and ignited with mercuric oxide (Gooch and Havens, Amer. J. Sci. 1896, 2, 416). (iv.) The separation of small quantities of aluminium from excess of iron has been successfully effected by the use of phenylhydrazine. The iron is first reduced to the ferrous condition by adding hydrochloric acid and ammonium bisulphite, and the solution almost neutralised with ammonia, a slight excess of phenylhydrazine is then added, and after one hour the aluminium hydroxide is collected and washed with a solution of phenylhydrazine sulphite. In this way

aluminium can be separated from iron, manganese, calcium, and magnesium (Hess and Campbell, J. Amer. Chem. Soc. 1899, 21, 776).

Separation of iron, aluminium, and phosphoric acid. When the total amount of these substances is small, the precipitate obtained by ammonia is ignited and weighed ($A=Fe_2O_3+Al_2O_3+P_2O_5$). The precipitate is then fused with sodium carbonate and silica, and the mass extracted with water containing a little ammonium carbonate. The residue containing iron and aluminium is evaporated down with sulphuric acid to dissolve the iron; the solution is reduced with hydrogen sulphide as in the preceding separation, and titrated with permanganate solution. The solution, which contains all the phosphoric acid, is evaporated down with hydrochloric acid to remove silica; the residue taken up with water, and the phosphoric acid precipitated from the filtrate as magnesium ammonium phosphate. From the weight of magnesium pyrophosphate obtained the amount of P_2O_5 is determined, and the Al_2O_3 is obtained by difference. If the total amount of these three substances is large, the original solution may be divided into three aliquot portions, in one of which the phosphoric acid is precipitated as ammonium phosphomolybdate, in the second part the iron is determined volumetrically, and from the third the total precipitate (Fe_2O_3, Al_2O_3,P_2O_5) is obtained (compare Cooksey, Analyst, 1908, 33, 437).

Chromium is readily separated from many metals, *e.g.* aluminium, by conversion into chromate, which is not precipitated by alkalis. This can be done in one of the following ways. (*a*) Make the solution alkaline with caustic potash or soda, saturate with chlorine, and then heat to expel excess of gas, and decompose hypochlorites by heating with ammonia. (*b*) Ammonium persulphate is added to a solution containing chromium, iron, and aluminium. On boiling, the chromium is oxidised to chromate, the acid set free during oxidation being sufficient to keep the iron and aluminium in solution (G. v. Knorre, Zeitsch. anorg. Chem. 1903, 16, 1097). (For the estimation of chromium in chromite and chrome steel, *see Volumetric section.*)

Aluminium from chromium. After chromium has been converted into chromic acid, the aluminium may be precipitated as hydroxide or as phosphate (*v. Determination of metals*). The filtrate is acidified, heated to boiling, and sodium thiosulphate added until the chromium is completely reduced; it can then be estimated as phosphate in the same way as aluminium.

Uranium is separated from the other metals of this group by the solubility of its hydroxide, sulphide, and acid uranates, in ammonium carbonate.

Uranium from iron and aluminium. An acid solution containing ammonium salts is mixed with excess of ammonium carbonate and ammonium sulphide in a closed flask. The precipitate contains ferrous sulphide and aluminium hydroxide; the uranium remains dissolved as the double carbonate $UO_2{\cdot}CO_3{,}2(NH_4)_2CO_3$. The filtrate is concentrated considerably, acidified with hydrochloric acid, boiled, and the uranium precipitated as ammonium diuranate with ammonia. The precipitate is ignited and weighed as U_3O_8. Or this oxide is heated with dilute sulphuric acid (1 : 6) at 170° in an inert atmosphere (carbon dioxide); the solution which contains uranyl sulphate (2 mols.) and uranous sulphate (1 mol.), is titrated with standard permanganate solution.

$$1\text{ c.c. }\tfrac{N}{10}KMnO_4=0{\cdot}03593U.$$

Uranium ores are treated in the following way. The mineral (0·5–1·0 gram) is dissolved in nitric acid or *aqua regia*, silica removed by evaporation, the soluble residue extracted with hydrochloric acid, and the metals of the copper group precipitated by hydrogen sulphide. The filtrate is oxidised with potassium chlorate, and treated successively with ammonium phosphate, ammonia (till nearly neutral), and sodium carbonate in excess. The mixture is boiled and sufficient ammonium chloride added to decompose excess of sodium carbonate. The precipitate, which contains the iron, vanadium, &c., is washed with aqueous ammonium carbonate. This salt is removed from the filtrate by boiling alone and with nitric acid. The solution is almost neutralised with ammonia, and to the boiling liquid are added successively microcosmic salt, sodium thiosulphate, acetic acid, and finally ammonium acetate. The precipitate, uranyl ammonium phosphate, is collected, ignited, moistened with nitric acid, again ignited and weighed as $(UO_2)_2P_2O_7$.

Uranium is separated from thorium (and iron) by means of hydroxylamine hydrochloride, which in ammoniacal solution precipitates thorium and ferric hydroxides, leaving the uranium in solution (Jannasch and Schilling, Chem. Zeit. 1905, 29, 248).

Cerium is separated *from other metals* by saturating the solution with sodium sulphate, this salt being added in fine powder. A crystalline double sulphate of cerium and sodium separates, and is washed with a saturated solution of sodium sulphate.

Glucinum is precipitated with aluminium in Group III., and separated from aluminium and the other metals of the group by one of the following methods: (i.) A saturated solution of sodium hydrogen carbonate dissolves out glucinum hydroxide from a precipitate containing aluminium and ferric hydroxides, leaving the latter unaffected (Parsons and Barnes, J. Amer. Chem. Soc. 1906, 28, 1589). (ii.) Aluminium and glucinum chlorides are separated by saturating their solutions with hydrogen chloride in the presence of ether; the former is precipitated, the latter remaining dissolved (Amer. J. Sci. [4] 11, 416). (iii.) The acetates may be separated by the use of hot glacial acetic acid, from which solvent basic glucinum acetate $Gl_4O(CO_2{\cdot}CH_3)_6$ separates on cooling (Parsons and Robinson; cf. also Glassmann, Ber. 1906, 39, 3366; and J. Amer. Chem. Soc. 1895, 17, 688).

Barium carbonate decomposes glucinum chloride, thus separating this metal from those of Group III*b*.

Vanadium is separated from the majority of metallic elements by fusion with sodium carbonate and potassium nitrate; the vanadium dissolves in water as sodium vanadate. Chromium and manganese would also be found in the aqueous extract, but from these metals

vanadium is separated by the addition of ammonium sulphide in excess, when chromium and manganese are precipitated respectively as hydroxide and sulphide leaving vanadium in solution as a thiovanadate (cf. Zeitsch. anorg. Chem. 5, 381; Compt. rend. 1904, 138, 810; and Hillebrand, Amer. J. Sci. [4] 6, 209). From arsenic, vanadium may be separated either by reducing with sulphur dioxide and precipitating arsenious sulphide with hydrogen sulphide or by heating the mixed sulphides in hydrogen chloride at 150°, when the arsenic is volatilised (Field and Smith, J. Amer. Chem. Soc. 1896, 18, 1051).

Vanadium is separated from phosphoric acid by reducing vanadic acid to a hypovanadic salt with sulphur dioxide, and precipitating the phosphorus as phosphomolybdate.

Vanadium and molybdenum are separated by the action of hydrogen sulphide on vanadic and molybdic acids under pressure, molybdenum sulphide being precipitated, or ammonium metavanadate may be precipitated by the action of excess of ammonium chloride (Gibbs, Amer. Chem. J. 1883, 5, 371); the latter method serves to separate vanadium from tungsten.

(For methods of estimating vanadium in iron and steel, *see* Brearley and Ibbotson, The Analysis of Steel Works Materials; and Blair, The Chemical Analysis of Iron.)

Tungsten is separated from the majority of other elements by fusion with alkali carbonate and extraction of the alkali tungstate with water. This extract, when acidified with nitric acid and evaporated to dryness, yields tungstic acid as a residue insoluble in water. From arsenic and phosphoric acids tungstic acid is separated by the addition of magnesia mixture, which precipitates the arsenic and phosphorus, leaving the tungstate in solution (Gooch, Amer. Chem. J. 1871, 1, 412; and Gibbs, *ibid.* 1885, 7, 337).

The tungsten in wolframite may be estimated by fusing the finely powdered ore (0·5 gram) with 6 parts of fusion mixture in a platinum crucible for half an hour. The fused mass is extracted with boiling water when alkali tungstate passes into solution together with silicate and stannate. The insoluble residue contains iron, manganese, calcium, and magnesium with small amounts of columbic and tantalic acids. The filtrate is evaporated to dryness with excess of nitric acid, and the residue, after heating at 120°, is extracted with dilute ammonium nitrate solution; the residue, which consists of tungstic oxide with silica and stannic oxide, is weighed and then treated with hydrofluoric acid and weighed again. This second residue consists of tungstic oxide and stannic oxide, and the latter is volatilised by heating repeatedly with ammonium chloride until the weight of the final residue (WO_3) is constant.

To remove tin the mixed oxides may be ignited with zinc powder, and the residue, after extraction with hydrochloric acid, is tungsten trioxide (Angenot, Zeitsch. angew. Chem. 19, 140).

(For other separations of tungsten from its usual associates, *see* J. Amer. Chem. Soc. 1900, 22, 772; Zeitsch. anorg. Chem. 1905, 45, 396; Zeitsch. anal. Chem. 1908, 47, 37; Bull. Soc. Chim. 1908, 13, 892.)

Columbium and *tantalum* are extracted from columbite or tantalite by fusing the mineral with potassium hydrogen sulphate and extracting the fused mass with hot water and hydrochloric acid. The residue is treated with ammonium sulphide to remove tin, tungsten, and again extracted with hot hydrochloric acid. The final residue is then dissolved in hydrofluoric acid, the filtered solution is treated with potassium carbonate: potassium tantalofluoride separates in acicular crystals and the mother liquor furnishes potassium columbium oxyfluoride, crystallising in plates (compare Weiss and Landecker, Zeitsch. anorg. Chem. 1909, 64, 65; and Chesneau, Compt. rend. 1909, 149, 1132).

Titanium. In addition to the process given under the estimation of titanium, this element may be separated from iron by the following methods: (i.) By adding ammonium sulphide to an alkaline tartrate solution of the two elements, when ferrous sulphide is precipitated (Gooch, Amer. Chem. J. 1885, 7, 283). (ii.) By precipitating titanic acid with phenylhydrazine (J. Amer. Chem. Soc. 1895, 25, 421). Titanium is separated from aluminium by boiling with an alkali acetate and dilute acetic acid, when basic titanium acetate is precipitated.

Titanium and *zirconium* are separated by the following methods: (i.) A solution of the elements in dilute sulphuric and acetic acids is boiled for some time, when titanic acid is precipitated (J. pr. Chem. 1869, 108, 75; Zeitsch. anal. Chem. 9, 388). (ii.) The acid solution is boiled with zinc till the titanium is reduced to titanous salt, the zirconium is then precipitated by the addition of potassium sulphate (Compt. rend. 1863, 57, 298). (iii.) A neutral solution of the nitrates is added drop by drop to a boiling concentrated solution of ammonium salicylate ($1 : 5H_2O$), the solution boiled for one hour, concentrated, and the precipitated zirconium salicylate collected and washed with ammonium salicylate solution. Titanium salicylate is soluble in hot water and remains in the filtrate (Dittrich and Freund, Zeitsch. anorg. Chem. 1907, 56, 337, 348).

Cerium is precipitated in the aluminium group (III.*a*), and, together with the other metals of the rare earths, is separated from iron and aluminium by means of oxalic acid or ammonium oxalate. From lanthanum, praseodymium, and neodymium it may be separated by suspending the hydroxides in aqueous caustic potash and passing in chlorine until the liquid is no longer alkaline. The cerium remains precipitated as the yellow hydrated dioxide, whilst the other hydroxides are dissolved (Mosander). Various methods have been proposed similarly based on the oxidation of cerous compounds to the ceric condition (*v.* Ann. Chem. Pharm. 131, 359; Monatsh. 1884, 5, 508; Ber. 35, 672).

Thorium, together with the rare earths, is separated from the other elements by oxalic acid. The further separation is effected by the following methods:—

(i.) Monazite sand is heated with concentrated sulphuric acid at 180°–200° for 2 to 3 hours, and the product taken up with water, and the rare earths precipitated by the addition of oxalic acid. The precipitated oxalates, after

washing till free from phosphoric acid, are ignited, and the resulting oxides dissolved in hydrochloric acid. The excess of acid is expelled by evaporation at 100°, the residue dissolved in water and treated with sodium thiosulphate. After 12 hours the solution is boiled for 10 minutes and filtered. The precipitate contains thorium, but contaminated with cerium; it is therefore redissolved and the precipitation repeated until the filtrate gives no precipitate on boiling with ammonia. At this stage the precipitate is ignited, fused with sodium hydrogen sulphate, the product dissolved in water, and the thorium finally precipitated with oxalic acid, the precipitate being ignited and weighed as ThO_2 (Fresenius and Hintz, Zeitsch. anal. Chem. 35, 543).

(ii.) The mixed oxalates obtained as before from the monazite sand are decomposed, and the metals converted into nitrates by repeated evaporation with nitric acid. The neutral solution of the nitrates is diluted with aqueous ammonium nitrate (10 p.c.) warmed to 80°, and the thorium precipitated as peroxide by the addition of pure hydrogen peroxide solution. The precipitate, which contains a trace of cerium peroxide, is filtered, washed with aqueous ammonium nitrate, ignited and weighed as ThO_2 (Benz, Zeitsch. angew. Chem. 1902, 15, 297; compare Chem. Zeit. 1908, 32, 509).

(iii.) Precipitation by organic acids. (*a*) Fumaric acid precipitates thorium fumarate in 40 p.c. alcohol, leaving the other rare earths in solution (Metzger, J. Amer. Chem. Soc. 1902, 24, 901). (*β*) *m*-Nitrobenzoic acid in aqueous solution precipitates its thorium salt, the separation being complete in the presence of aniline. Under these conditions, cerium, praseodymium, neodymium, and lanthanum remain in solution (Kolb and Akele, Zeitsch. angew. Chem. 1905, 18, 92).

(iv.) Boiling with potassium azide in neutral solution leads to the precipitation of thorium hydroxide, the salts of the other rare earth metals being unaffected (Dennis, J. Amer. Chem. Soc. 1896, 18, 947). Fusion with potassium hydrogen fluoride separates thorium and cerium from zirconium; for on extraction with water containing a little hydrogen fluoride, potassium zirconofluoride dissolves, leaving behind the fluorides of thorium and cerium (Chem. News, 1897, 75, 230).

Manganese and *iron* are separated in their alloys (ferromanganese, &c.) by dissolving the alloy in hydrochloric acid with a little nitric acid. After boiling off nitrous fumes, the solution is filtered and diluted with boiling water to 600 c.c. Ammonia is added till a faint turbidity remains, excess of neutral ammonium acetate is then quickly added, and the solution boiled. The basic ferric acetate thus precipitated contains some manganese; it is therefore redissolved and the separation repeated. The united filtrates are treated with excess of bromine followed by strong ammonia also in excess; the liquid is vigorously agitated during the addition of these reagents, and then heated slowly to boiling. The precipitate is collected, washed with boiling water, ignited and weighed as Mn_3O_4 (compare Riggs, Amer. J. Sci. 43, 135; Gooch, Zeitsch. anorg. Chem. 1898, 17, 268; Brearley and Ibbotson, Chem. News, 1902, 82, 209; Zeitsch. anal. Chem. 1904, 43, 382; Jannasch and Rühl, J. pr. Chem. 1905, 72, 1; Moore and Miller, J. Amer. Chem. Soc. 1908, 30, 593).

Nickel from cobalt. The solution, which should contain but little free acid, is mixed with excess of pure potassium cyanide free from cyanate (the ordinary cyanide is fused with charcoal, dissolved in water, filtered, and evaporated in a silver dish), heated to boiling, and mixed with a solution of mercuric oxide in mercuric cyanide. The precipitate, when washed, dried, and ignited, leaves a residue of nickel oxide NiO, which is weighed. Cobalt is usually determined by difference; but if direct estimation is required, the filtrate from the nickel is evaporated to dryness, heated for some time with strong sulphuric acid, and the cobalt estimated in the solution.

Nickel can be separated from cobalt and all the other metals of Groups III. and IV. by precipitation in ammoniacal or dilute acetic acid solution with dimethylglyoxime (*see Estimation of nickel*). If ferric salts are present, they should be reduced to the ferrous condition, or tartaric acid is added before rendering the solution alkaline; the organic acid prevents the co-precipitation of iron, chromium, and aluminium (Brunck, Zeitsch. angew. Chem. 1907, 20, 1845).

Cobalt from nickel. (i.) In acetic acid solution, nitroso-*β*-naphthol precipitates the cobalt as cobaltic nitroso-*β*-naphthoxide (Ilinski and Knorre, Ber. 18, 699). (ii.) Cobaltic hydroxide is precipitated from a neutral solution of the two metals by barium carbonate and bromine water (Taylor, Proc. Manchester Phil. Soc. 1902, 46, (ii.) 1). (iii.) Small quantities of cobalt can be detected and estimated in the presence of nickel by adding to a neutral solution concentrated aqueous ammonium thiocyanate. On shaking with amyl alcohol and ether, these organic solvents extract the double salt $(NH_4)_2Co(CNS)_4$ (blue solution), leaving the nickel in the aqueous solution (Ber. 1901, 34, 2050 and 3913). Zinc is also removed with the cobalt.

Cobalt is precipitated as double nitrite on adding potassium nitrite to an acetic acid solution of the two metals; the nickel is left in solution (Fischer, Pogg. Ann. 72, 477; and Funk, Zeitsch. anal. Chem. 1907, 46, 1).

Separation of zinc, manganese, nickel, and cobalt. The slightly acid solution of the four metals is treated with sodium carbonate till a permanent precipitate is formed, which is redissolved by a few drops of hydrochloric acid; then for every 100 c.c. of liquid 15 drops of the same acid are added, followed by 10 c.c. of 20 p.c. ammonium thiocyanate; the solution heated to 70° is then saturated with hydrogen sulphide; the zinc in the precipitate is determined either as sulphide or oxide. Manganese is separated from nickel and cobalt by passing hydrogen sulphide into a solution of their salts in acetic acid containing excess of ammonium acetate, when nickel and cobalt are precipitated as sulphides; the filtrate may, however, still contain small amounts of these metals. The solution is concentrated, treated with ammonium sulphide, and then with acetic acid. A further precipitate of nickel and cobalt sulphides is thus obtained (*v.* Treadwell and Kramers, Zeitsch. anorg. Chem. 1901, 26, 184; compare

J. Soc. Chem. Ind. 1905, 24, 228; Bull. Soc. Chim. 1908, (iv.) 3, 114).

Zinc from nickel and cobalt. Add excess of pure potassium cyanide and precipitate the zinc with sodium sulphide.

GROUP IV.—The metals of this group are separated from those of the following group by precipitation with ammonium carbonate (*v. General methods of estimation*). The liquid is first made alkaline with ammonia and afterwards heated to boiling to ensure complete precipitation.

Barium from calcium and strontium. The dilute neutral or feebly acid solution is mixed with excess of freshly prepared hydrofluosilicic acid and one-third its volume of 95 p.c. alcohol allowed to stand twelve hours, collected on a weighed filter, washed with a mixture of equal parts of water and alcohol, and dried at 100°. Calcium and strontium are not precipitated.

Barium from strontium. Ammonium bichromate and ammonium acetate are added alternately to a solution of barium and strontium salts containing ammonium acetate. After three hours the precipitate, $BaCrO_4$, is washed with ammonium acetate solution, dried at 180°, and weighed (Kahan, Analyst, 1908, 33, 12; *v.* Zeitsch. anal. Chem. 1905, 44, 742; J. Amer. Chem. Soc. 1908, 30, 1827).

Barium and strontium from calcium. The solution is mixed with a concentrated solution of ammonium sulphate, using 50 parts of the latter salt for one part of the mixed salts, heated to boiling with addition of a small quantity of ammonia, and the precipitate washed with water containing ammonium sulphate. The filtrate contains the calcium, which can be precipitated by ammonium oxalate.

Calcium from strontium. Convert the metals into nitrates, evaporate to dryness, and extract with a mixture of equal volumes of alcohol and ether, which dissolves calcium nitrate but not strontium nitrate.

Calcium from strontium and barium. The nitrates are dried at 140° and extracted with amyl alcohol, which dissolves out the calcium salt, leaving the other two undissolved (Browning, Amer. J. Sci. 43, 50, 314).

Calcium from magnesium. The calcium is precipitated by ammonium oxalate (*v. Determination of metals*), adding sufficient of this salt to convert both metals into oxalates, since calcium oxalate is appreciably soluble in a solution of magnesium chloride. In very accurate separations the precipitate should be filtered off, redissolved in hydrochloric acid, and reprecipitated by adding excess of ammonia and a small quantity of ammonium oxalate (*cf.* Richards, Zeitsch. anorg. Chem. 1901, 28, 71; Zeitsch. angew. Chem. 1908, 21, 592; J. Amer. Chem. Soc. 1909, 31, 917).

GROUP V.—*Magnesium from alkalis.* The magnesium is precipitated with ammonium phosphate in the usual way, the filtrate evaporated to dryness, heated to expel ammonium salts, the residue evaporated two or three times with strong nitric acid to remove hydrochloric acid, and the phosphoric acid removed by stannic oxide (*v. Phosphoric acid from metals*; *v.* Gibbs, Amer. J. Sci. [3] 5, 114; Neubauer, Zeitsch. angew. Chem. 1896, 9, 439; Gooch, Zeitsch. anorg. Chem. 1899, 20, 121).

In solutions free from ammonium salts, the magnesium can be precipitated as magnesium hydroxide by the addition of aqueous barium hydroxide. The excess of barium is removed by ammonium carbonate and the alkalis are determined in the filtrate. Magnesium chloride is also separated from the alkali chlorides by ignition with mercuric oxide, when mercuric chloride and the excess of oxide volatilise, leaving magnesia, from which the soluble alkali chlorides are readily separated.

Alkalis from magnesium. (*a*) The solution is made distinctly alkaline with pure milk of lime (calcium hydroxide suspended in water) and boiled for some time, care being taken that it remains alkaline. The liquid is filtered, made alkaline with ammonia, and the calcium precipitated by adding ammonium carbonate and a small quantity of ammonium oxalate. The filtrate is acidified with hydrochloric acid and evaporated in a weighed platinum dish, heated to expel ammonium salts, and the alkaline chlorides weighed. They should dissolve completely in water and should give no precipitate when mixed with ammonium carbonate and allowed to stand for some time. If any calcium is present, it must be removed by repeating the treatment with ammonium carbonate and oxalate.

(*b*) The solution, which must contain only potassium, sodium, and magnesium, is mixed with excess of oxalic acid, evaporated to dryness, and the oxalic acid expelled by heating carefully over a lamp until white fumes cease to come off. The residue is treated with water, when potassium and sodium dissolve as carbonates, whilst magnesium oxide remains undissolved.

Alkalis from silicates. (*a*) The finely powdered silicate (1 gram) is mixed intimately with an equal weight of ammonium chloride and eight parts of dense granular calcium carbonate, and heated to redness for half an hour. The product is boiled with water in a platinum or silver dish for two hours, care being taken to make up the loss by evaporation, the liquid is filtered and the residue well washed with hot water. The filtrate, which contains calcium and the alkalis, is treated in the manner just described. In this method of decomposition, which is due to J. Lawrence Smith, the silicate is decomposed by the calcium oxide, which is dissolved by the fused calcium chloride formed by the action of the ammonium chloride on the calcium carbonate.

(*b*) The silicate is treated in a platinum dish with excess of sulphuric and hydrofluoric acids, and the mixture evaporated on the water-bath until the mineral is entirely decomposed. The temperature is then raised to drive off the greater part of the sulphuric acid, and the cooled residue extracted with water. The sulphates are converted into chlorides by barium chloride, the metals of Groups III. and IV. precipitated by ammonia and ammonium carbonate, the magnesium removed by barium hydroxide, and the excess of this reagent eliminated by ammonia and ammonium carbonate. The alkali chlorides remaining in the final filtrate are estimated as indicated in the following section. Certain native silicates of the andalusite group are not decomposed completely by this treatment with hydrofluoric acid; these minerals

may, however, be broken up by ignition with ammonium fluoride.

(c) The alkali and other metals contained in a refractory silicate may be separated by heating the mineral with lead carbonate. The product is extracted with nitric acid; the lead removed as chloride and sulphide, and the metals in solution dealt with in the customary manner (Jannasch, Zeitsch. anorg. Chem. 1895, 8, 364).

(d) Silicates of different types are decomposed by fusion with boric anhydride followed by extraction with methyl alcoholic hydrogen chloride and evaporation to remove the boric acid as volatile methyl borate (Ber. 1895, 28, 2822; Zeitsch. anorg. Chem. 1896, 12, 208).

Potassium from sodium. The metals are converted into chlorides, which are evaporated to dryness and weighed together after drying at 150°. The salts are dissolved in water, mixed with platinic chloride in sufficient quantity to convert both into platinichlorides, and evaporated nearly but not quite to dryness. The residue is then treated with alcohol, which dissolves the sodium but not the potassium salt (*v. Potassium*). If the mixture is evaporated to complete dryness and heated so that the sodium platinichloride becomes anhydrous, it dissolves with difficulty in alcohol. Under some conditions reversion takes place and sodium chloride separates in white crystals insoluble in alcohol. In this case the alcohol is very carefully evaporated and the residue again treated with platinic chloride.

In order to separate small quantities of potassium from large quantities of sodium, advantage may be taken of the fact that potassium chloride is more soluble than sodium chloride in strong hydrochloric acid (Zeitsch. analyt. Chem. 1880, 156). The dry mixed chlorides are thoroughly moistened with concentrated hydrochloric acid: 2 c.c. of the acid is then added, and the salt thoroughly crushed and stirred with a glass rod. After standing for a few minutes the acid is poured off into a small dish. Ten repetitions of this treatment, using 2 c.c. of acid each time, will suffice to remove all potassium, whilst the greater part of the sodium chloride is not dissolved. The acid solution is evaporated to dryness and the potassium determined as platinichloride (Chem. Soc. Trans. 39, 506). By adopting this plan much less platinic chloride is required, and the separation is much more accurate.

Lithium from sodium and potassium. When a lithia-containing silicate (*e.g.* lepidolite) is broken up by one of the preceding processes the precipitable metals of Groups I.–IV. are first removed and the alkali metals converted into chlorides. The combined chlorides are dried and weighed; potassium is estimated in one portion, and in a second portion the lithium is estimated by extracting the chlorides with amyl alcohol or with ether-alcohol saturated with hydrogen chloride. Anhydrous lithium chloride is soluble in these media, whereas sodium and potassium chlorides are practically insoluble therein. Lithium chloride has also been separated from the chlorides of the other alkali metals and barium by dissolving it in boiling pyridine, in which the others are insoluble (Kahlenberg and Krauskopf, J. Amer. Chem. Soc. 1908, 30, 1104). (For the separation of lithium as phosphate and fluoride, *see* Ann. Chim. Phys. 98, 193; Frdl. 29, 332, and Analyst, 16, 209.)

Rubidium and *cæsium* are separated from each other and from potassium by taking advantage of the difference in the solubility of their platinichlorides. Rubidium hydrogen tartrate is more than nine times less soluble than the cæsium salt. Cæsium carbonate alone of the alkali carbonates is soluble in alcohol. Cæsium gives rise to a series of sparingly soluble perhalides and yields double chlorides with lead and antimony chlorides (*v.* Wells, Amer. J. Sci. 43, [3] 17; and Amer. Chem. J. 1901, 26, 265).

Ammonium salts can be removed from a solution in two ways: (1) By evaporating to dryness and carefully heating over a lamp until all fumes cease to come off. (2) By concentrating the solution and heating for some time with excess of strong nitric acid. When evolution of oxides of nitrogen ceases, the liquid is evaporated to complete dryness and the nitrates converted into chlorides by repeated treatment with hydrochloric acid if necessary.

B. *The Estimation of Acid Radicles.*

Bromine from chlorine. (a) The two elements are precipitated by excess of silver nitrate and weighed together. The filter ash is removed, the precipitate cautiously heated to fusion, and a portion poured into a weighed porcelain boat. The boat is again weighed, heated to fusion in a current of dry chlorine in a glass tube until all bromine is expelled, and the silver chloride formed is weighed. It is advisable to heat in chlorine for a further period of ten minutes and weigh again. The loss of weight multiplied by 4·223 gives the amount of silver bromide in the weight of precipitate treated with chlorine, from which the quantity in the whole precipitate is readily calculated (*v. Indirect methods of determination*).

This method gives accurate results if the proportion of bromine is not too small. When a small quantity of bromine is mixed with a large quantity of chlorine, the former may be concentrated by taking advantage of the fact that if a limited quantity of silver nitrate is added, the precipitate will contain all the bromine, but only a portion of the chlorine. In one portion of the substance the two elements are determined together by complete precipitation. Another portion in somewhat dilute solution is mixed with a quantity of silver nitrate insufficient for complete precipitation, and allowed to stand in the cold for some time with repeated agitation. The precipitate is collected, washed, and weighed, and the proportion of bromine determined in the manner already described. The quantity of silver nitrate which should be used depends upon the relative proportions of chlorine and bromine. If one part of bromine is present for every 1000 parts of chlorine, one-fifth or one-sixth of the silver necessary for complete precipitation should be used; if one part to 10,000, only one-tenth; if one part to 100,000, only one-sixtieth (Fehling).

(b) The solution of the two halides heated at 70°–80° is treated with ammonium persulphate, and the liberated bromine volatilised in a current of air, collected in sulphurous acid, and

estimated as silver bromide (Engel, Compt. rend. 1894, 118, 1263).

Iodine is separated from chlorine in exactly the same way as bromine from chlorine. The loss of weight on treating with chlorine, multiplied by 2·569, gives the weight of silver iodide in the portion of precipitate taken.

Iodine from chlorine or bromine. The solution is slightly acidified with hydrochloric acid, mixed with palladious chloride until precipitation is complete, and allowed to stand in a warm place for twenty-four or forty-eight hours. The precipitate of palladious iodide PdI_2 is collected on a weighed filter, washed with warm water, and dried at 100°, or is reduced by heating in hydrogen and the metal weighed.

Iodine can also be liberated by nitrous acid and estimated volumetrically (*v. Volumetric methods*).

Bromine, chlorine, and iodine from one another. (*a*) The three elements are precipitated and weighed together in one part of the solution. In another part the iodine is separated as palladious iodide by palladious chloride, or better, nitrate; the excess of palladium is removed by hydrogen sulphide and excess of the latter by ferric sulphate; and the chlorine and bromine in the filtrate are precipitated completely or fractionally and the bromine determined in the manner previously described. The chlorine is estimated by difference.

(*b*) A direct method of estimating the three halogens in a mixture of their soluble salts has been investigated by Jannasch and his collaborators. The process in its present stage of development gives a sharp separation of chlorine and iodine, but the results for bromine are rather low. The mixture dissolved in 25 c.c. of water is heated to boiling with acetic acid and hydrogen peroxide, and the liberated iodine expelled by a current of carbon dioxide. The bromine is then liberated by adding excess of hydrogen peroxide and moderately strong sulphuric acid (5 : 3). The iodine is collected in an ammoniacal solution of hydrazine sulphate and the bromine in alkaline hydrazine sulphate. After acidifying with nitric acid, the iodine and bromine are precipitated as silver salts, and the chlorine left in the distilling flask is similarly precipitated (Ber. 1906, 39, 196, 3655; J. pr. Chem. 1908, 78, 29; Zeitsch. anorg. Chem. 1, 144 and 245). (For other processes for separating the halogens, *see Volumetric section*; and Monatsh. 13, 1; Chem. Soc. Trans. 1893, 63, 1051; Compt. rend. 1898, 126, 187; Ber. 1899, 32, 3615.)

Several indirect methods of estimating these three elements in a mixture have been proposed. They are based on the methods given, together with the fact that the radicles may be precipitated exactly by a standard solution of silver nitrate and the precipitate weighed, the proportion of silver and halides in the precipitate being thus determined (*v.* Fresenius, Quantitative Analysis, sect. 5).

Indirect Methods of Determination. This estimation of two or three halogens in a mixture furnishes a good example of indirect methods of analysis, which are adopted in those cases where the separation of two or more constituents is either impossible or inconvenient. The calculation of the relative proportions of these constituents becomes possible when one can obtain as many independent relationships as there are radicles to be determined. The estimation of chlorine and bromine (*a*) is a case in point. The loss of weight due to the replacement of Br.(79·92) by Cl(35·46) is proportional to the amount of bromine present. Let w = loss of weight. Now

$$\frac{\text{Cl}}{\text{Br}} = \frac{35{\cdot}46}{79{\cdot}92} \text{ and hence } \text{Br} - \frac{35{\cdot}46}{79{\cdot}92}\text{Br} = w;$$

or Br = 1·797 w: *i.e.* the loss of weight multiplied by 1·797 gives the quantity of bromine present.

Similarly, the halogens in a mixture of soluble chloride, bromide, and iodide can be calculated from the following data: (i.) the amount of iodine present, set free by nitrous acid or hydrogen peroxide and acetic acid; (ii.) the total weight of mixed silver halides obtained from a known amount of mixture; (iii.) the silver required for the complete precipitation of the three halogens; this is obtained volumetrically. The indirect method can also be applied to the estimation of sodium and potassium contained in the mixed chlorides from a silicate analysis (*v. supra*). The data required are: (i.) the weight A of mixed chlorides; (ii.) the weight B of chlorine therein contained, this amount being determined either gravimetrically or volumetrically. Let x and y be the amounts of potassium and sodium respectively, then these quantities are readily calculated from the following equations, where Cl, K, and Na represent the atomic weights of these elements.

$$x + y = \text{A} - \text{B}$$
$$\frac{\text{Cl}}{\text{K}}x + \frac{\text{Cl}}{\text{Na}}y = \text{B}$$

These indirect methods give useful results only when the atomic or molecular weights of the two radicles differ considerably, and when the quantities present are approximately equal. Moreover, the results are affected to a considerable extent by comparatively small experimental errors.

Cyanide from chloride. Silver nitrate is added in excess to an approximately 2 p.c. solution of soluble cyanide and chloride. An excess of normal nitric acid is now added, and the mixture containing the freshly precipitated silver salts is distilled, when hydrocyanic acid is expelled quantitatively and estimated in the distillate by precipitation as silver cyanide with acidified silver nitrate, drying this precipitate at 110°, and weighing in a Gooch crucible or on a tared filter paper (Plimmer, Chem. Soc. Trans. 1904, 85, 12; compare also Richards and Singer, Amer. Chem. J. 1902, 27, 205).

Phosphoric acid from metals. (*a*) The nitric acid solution, as free as possible from hydrochloric acid, and free from silicic and arsenic acids, is mixed with excess of a solution of ammonium molybdate in nitric acid, heated gently for a few minutes, and filtered after standing for a short time. The precipitate is washed with dilute nitric acid, dissolved in ammonia, and the phosphoric acid precipitated by magnesia mixture. This method is more especially applicable when the quantity of phosphoric acid is relatively small. To prepare ammonium

molybdate solution, 25 grams of the salt is dissolved in 100 c.c. of dilute ammonia, and the solution poured gradually with constant and vigorous agitation into 500 c.c. of a mixture of 3 vols. strong nitric acid and 1 vol. water. The liquid is heated at 50° for some time and the clear solution drawn off.

(*b*) By stannic oxide. The nitric acid solution is concentrated, mixed with fuming nitric acid boiling at 86°, heated gently, and granulated tin added gradually in quantity not less than four times the amount of phosphoric acid present. The stannic oxide produced forms an insoluble compound with the phosphoric acid. This is filtered off, washed with hot water, dissolved in caustic potash, the solution saturated with hydrogen sulphide, acidified with acetic acid, and the stannic sulphide removed. The filtrate is concentrated, any stannic sulphide which separates subsequently is removed, and the phosphoric acid is estimated in the usual way. The original filtrate from the stannic oxide contains the metals previously combined with the phosphoric acid.

(*c*) The nearly neutral solution is mixed with silver nitrate and digested for some time with excess of silver carbonate. The phosphoric acid separates as silver phosphate, the metals remain in solution with the excess of silver nitrate. The silver is removed by hydrochloric acid.

(*d*) When the phosphoric acid is combined with metals which form phosphates insoluble in water but soluble in acetic acid, the solution is nearly neutralised, mixed with sodium or ammonium acetate, and a slight excess of ferric chloride containing a known weight of iron added. The liquid is heated to boiling, the mixture of ferric phosphate and basic acetate washed with hot water, dried, and heated in a platinum crucible until the weight is constant. The weight of the precipitate *minus* the known weight of the ferric oxide gives the phosphoric anhydride P_2O_5. The precipitate may be moistened with nitric acid before the final ignition.

Phosphoric acid in silicates. In the analysis of silicates (*v. supra*) the phosphoric acid is found together with iron and aluminium in the precipitate produced by ammonia in the filtrate from the silica. This mixture is analysed in accordance with the method indicated under the separations of metals (Group III.).

Phosphorus and silicon in iron and steel. The iron or steel borings are dissolved in nitric acid ($1HNO_3$ sp.gr. $1{\cdot}4 : 1H_2O$); the solution evaporated to dryness, and the residue ignited carefully until all the ferric nitrate is converted into ferric oxide. The ignited residue is dissolved in concentrated hydrochloric acid heated nearly to boiling, when the ferric oxide and phosphate pass into solution, leaving insoluble silica. The solution is evaporated to dryness, moistened with strong hydrochloric acid, and taken up with water; the silica is collected, ignited, and weighed, its purity being tested by treatment with hydrofluoric and sulphuric acids. The phosphoric acid in the filtrate is estimated by either of the following methods.

(*a*) The ferric solution, diluted and almost neutralised with ammonia, is reduced with sulphurous acid or sodium sulphite. Hydrochloric acid is added and the excess of sulphur dioxide expelled by boiling. A small portion of the ferrous iron is now reoxidised with a few drops of bromine water. Ammonia is added carefully till a brown precipitate is formed which becomes green on stirring. Acetic acid is added till the precipitate either dissolves or becomes whiter, and the solution then heated to boiling. The precipitate, which contains all the phosphorus as ferric phosphate mixed with basic ferric acetate, is dissolved in hydrochloric acid, the solution evaporated nearly to dryness, excess of citric acid added, and then magnesia mixture and ammonia. The magnesium ammonium phosphate is redissolved in hydrochloric acid and reprecipitated in the presence of citric acid to remove a small amount of iron, and ignited and weighed as $Mg_2P_2O_7$.

(*b*) The filtrate from the silica is evaporated to dryness, the residue dissolved in dilute nitric acid, ammonium nitrate added, and the solution heating to boiling. A boiling solution of ammonium molybdate is then added to phosphate solution, when ammonium phosphomolybdate is precipitated quantitatively. This precipitate is redissolved in ammonia to which ammonium nitrate and ammonium molybdate are added, and reprecipitated by adding hot nitric acid to the boiling solution. The compound is now pure, and is collected, washed with water containing ammonium nitrate and nitric acid, and either dried at 160°–180° or gently ignited. In the former case it is weighed as $(NH_4)_3PO_4$, $12MoO_3$ (containing 3·782 p.c. P_2O_5) or in the latter as $P_2O_5{,}24MoO_3$ (containing 3·946 p.c. P_2O_5) (*v.* Ber. 1878, 11, 1640; Zeitsch. anorg. Chem. 1893, 32, 144; Amer. Chem. J. 34, 204; Analyst, 1909, 34, 392; Chem. Zeit. 21, 442). Separation of phosphoric and titanic acids (*v.* J. Soc. Chem. Ind. 1895, 14, 443). Estimation of phosphorus in phosphor-bronze (*v.* J. Amer. Chem. Soc. 1897, 19, 396) in phosphor-tin (J. Soc. Chem. Ind. 1908, 27, 427).

Silicic acid from titanic acid. The silica and titanium dioxide are weighed together, the mixture fused with a somewhat large quantity of potassium hydrogen sulphate, and the cooled mass extracted with water. Silica is left undissolved, titanic oxide dissolves, and can be precipitated from the filtrate by ebullition (*v. Titanium*).

Sulphides. If the sulphides are decomposable by hydrochloric acid, the hydrogen sulphide is absorbed in hydrochloric acid containing bromine (*v. Determination of metals*). Insoluble sulphides are decomposed by gently heating with *aqua regia* or with hydrochloric acid and bromine, and the sulphuric acid estimated in the solution. The latter method gives the total sulphur.

Sulphur in coal and coke. The finely powdered material (1 gram) is mixed intimately with 1 gram of calcined magnesia and 0·5 gram of sodium carbonate, and ignited to dull redness in an open platinum crucible for 1 hour, the mixture being stirred every five minutes with a platinum wire. The mixture is then heated strongly for 10 minutes with 1 gram of ammonium nitrate. The residue is extracted with water and the sulphate determined in the usual way (Eschka). The sulphur may also be determined by heating the coal with sodium or potassium carbonate (4 parts) alone, and extracting

the residue with hydrochloric acid and a few drops of bromine (Nakamura). (Compare also Zeitsch. angew. Chem. 1905, 18, 1560; Chem. Zeit. 1908, 32, 349; J. Russ. Chem. Soc. 1902, 34, 457.)

Sulphur in pyrites. The pyrites is oxidised either by fusion with sodium peroxide and sodium carbonate or by oxidation with nitric acid and bromine. These processes convert the sulphur to sulphate, which is estimated in the usual way (*v.* J. pr. Chem. 1892, [2] 45, 103; Zeitsch. anorg. Chem. 6, 303, *l.c.* 1896, 12, 129; J. Soc. Chem. Ind. 1905, 24, 7; Chem. News, 1906, 93, 213).

Sulphuric acid from all other acids except hydrofluosilicic by precipitation with barium chloride in presence of hydrochloric acid.

Sulphuric acid from hydrofluosilicic acid. The solution is mixed with excess of potassium chloride and an equal volume of strong alcohol, filtered through a weighed filter, and the precipitate of potassium silicofluoride (K_2SiF_6), washed with a mixture of equal volumes of alcohol and water, and dried at 100°. The sulphuric acid in the filtrate is estimated in the usual way after evaporation of the alcohol.

Titanic acid from silicic acid (*v. Silicic acid from titanic acid*).

Boric acid. The borates of the alkali and alkaline earth metals, when heated with pure methyl alcohol (free from acetone) and acetic acid, evolve all the boron present in the form of methyl borate (b.p. 65°). This liquid, when added to moist lime, is completely hydrolysed and the boric acid set free combines with the calcium oxide forming calcium borate. The decomposition is effected in a small retort fitted with a tap funnel for introducing further quantities of methyl alcohol. The retort is connected with a water condenser and a conical flask containing a weighed amount of quicklime. This lime is carefully slaked before the distillation, and the methyl borate dropping into the conical flask is decomposed and the boric acid taken up by the lime. The contents of the receiver are rinsed into a platinum dish, and the methyl alcohol evaporated at as low a temperature as possible. The residue is cautiously ignited to destroy calcium acetate, and the increase in weight of the lime represents the amount of boric anhydride B_2O_3 obtained from the borate. Instead of lime, aqueous ammonium carbonate may be used in the receiver, and the liquid poured on to slaked lime (from a known weight of quicklime) contained in a platinum dish (Zeitsch. anal. Chem. 1887, 26, 18, 364).

Volumetric Methods.

In volumetric analysis the proportion of a substance is ascertained, not by separation and weighing, but by determining the exact volume of a reagent solution of known concentration required to produce some particular reaction, such as neutralisation, oxidation, or precipitation. The termination of the reaction is indicated by some end-reaction, which is usually a production, destruction, or change of colour, the formation of a permanent precipitate or the cessation of the formation of a precipitate. In determining the strength of caustic soda, for example, it is coloured yellow with methyl orange, and a dilute solution of sulphuric acid of known strength is added gradually until the yellow colour of the methyl orange just changes to red, thus indicating the point of neutralisation. The volume of acid required is noted; the weight of sulphuric acid which it contains, and hence the weight of soda which it will neutralise, is known, and thus the proportion of soda in the substance is determined.

In order that a reaction may serve as the basis of a volumetric process, it must be rapid, simple, and definite, and not complicated by secondary reactions. It should remain constant through considerable variations in conditions, and should not, for example, be materially affected by the degree of concentration of the solution. A final reaction should be rapid, perfectly decisive, and should only require a slight excess of the reagent for its production. In many cases a third substance is employed to indicate the completion of the reaction, and is termed an *indicator.* It is an *internal indicator* if it is added to the bulk of the liquid, an *external indicator* if drops of the liquid are removed and brought in contact with it.

The execution of volumetric processes involves the possession of accurately graduated instruments of three kinds, viz. flasks, pipettes, and burettes. The flasks should be fitted with well-ground stoppers, and should have somewhat long necks, the graduation being not higher than the middle of the neck, in order that there may be sufficient empty space for efficient agitation. Flasks holding respectively 1000 c.c., 500 c.c., 250 c.c., and 100 c.c., are used. Each flask should have two graduation marks, viz. the *containing mark,* indicating the point to which the flask must be filled in order that it may then contain the particular volume of liquid, and the *delivery mark* or point to which the flask must be filled in order that it may deliver the given volume of liquid when emptied by draining. A pipette is usually a cylindrical bulb terminating at each end in a tube, the lower of which is drawn out to a jet, whilst the end of the upper tube is slightly contracted so that it may be readily closed by the forefinger and the flow of liquid regulated or stopped altogether. Usually a pipette has only a *delivery* mark, but occasionally they are graduated throughout their whole length, and then take the form of a somewhat wide tube contracted to a jet at the bottom and terminating in a narrower tube at the top. Pipettes of 100 c.c., 50 c.c., 25 c.c., 10 c.c., and 5 c.c. capacity are most generally useful. A burette is a long tube of uniform bore, 12 to 15 mm. in diameter, graduated in cubic centimetres and tenths or fifths. A convenient capacity is 50 c.c. It is open at the top and contracted at the lower end, to which a glass jet is attached by means of a piece of narrow indiarubber tubing. This tubing is nipped by a spring pinchcock, which is opened by the pressure of the fingers, the flow of liquid being thus regulated. A better plan is to insert in the indiarubber tubing a short piece of glass rod the diameter of which is just sufficient to prevent the flow of liquid when the tubing remains circular. If, however, the tubing is squeezed out laterally by the pressure of the thumb and fore finger (Fig. 9), a channel

Fig. 9.

is made through which the liquid can pass, and by increasing or reducing the pressure, the flow of liquid can be regulated to a nicety. Certain reagents act upon indiarubber, and for these a burette with a glass stopcock should be used. This form is, in fact, the most convenient for all purposes. The stopcock may be prevented from sticking by a little vaseline or paraffin, and from slipping out by a small indiarubber ring passed over the tap and round the burette tube. Sometimes the tube carrying the stopcock is not in the same line with the burette, but is bent twice at right angles, so that the burette jet, although still vertical, is one or two inches in advance of the burette itself. This form is useful when titrating hot liquids, since the risk of heating the burette and its contents is reduced. An alternative method is to have the top of an ordinary burette funnel-shaped, which admits of the burette being slung in a stand by the funnel without other support, so that it can be tilted from the vertical when titrating hot solutions.

When a burette is in use, it is important that it should be supported in a vertical position. This can be done by means of a clamp attached to a stand similar to a retort stand. A useful and easily constructed burette stand is described in J. Amer. Chem. Soc. 1905, 27, 1442.

When several different solutions are being used continually, it is convenient to have the series of burettes attached to a revolving stand, so that each may be brought round to the front when required. Short test-tubes inverted over the tops of burettes serve to keep out dust.

Standard solutions should be kept in well-stoppered bottles in a cool place protected from bright light. When many determinations of the same kind have to be made, it is convenient to keep the reservoir of standard solution attached to the burette to facilitate the filling of the latter. A glass T-piece is introduced between the graduated part of the burette and the stopcock or pinchcock, and is attached by means of an indiarubber tube to a tubulus at the bottom of the bottle which contains the standard solution and stands on a shelf above the burette. If this bottle has no tubulus, a glass tube bent twice at right angles, with one limb reaching to the bottom of the bottle and the other connected with the burette, is fitted into the neck of the bottle by means of a cork, and is kept always full, so that it acts as a siphon. There must, of course, be an entrance for air as the liquid flows from the bottle. The flow of liquid into the burette is regulated by a pinchcock on the indiarubber tube. If the standard solution acts upon indiarubber, all these connections must be constructed of glass tubing. Burettes may now be obtained fitted with Greiner and Friedrich's three-way taps (compare Fig. 12); these are readily connected to reservoirs and filled from the bottom. Filling the burette from the bottom avoids the formation of air-bubbles, but it can also be filled from the top if the tube from the stock bottle is bent slightly so that the liquid flows down the side of the burette. A convenient form of apparatus for this method, which is the only one available with an ordinary tap burette without a side-tube attachment, is described in Chem. News, 1906, 93, 71. When the standard solution alters if exposed to air, the surface of the liquid may be covered with a layer of rectified paraffin of moderately high boiling-point, or the neck of the bottle may be provided with a cork carrying a tube containing caustic potash, or alkaline pyrogallate, through which all air entering the bottle has to pass. A still better plan is to fill the upper part of the stock bottle with carbon dioxide, or, if the nature of the solution permits, with coal gas, and connect it by means of a cork and tube with a self-acting carbon dioxide apparatus or the ordinary gas supply. When solution is withdrawn, carbon dioxide or coal gas enters. The burette should be kept permanently attached to the reservoir as just described, and the top end of the burette also put into communication with the inert gas supply.

Graduation of the instruments.—Accurate calibration of the measuring vessels is of course necessary if correct results are to be obtained, and it is never advisable to trust the makers' graduations. All the instruments should be checked before being taken into use. Although it is sufficient for most purposes if the relative volumes of the vessels are correct, they should nevertheless be graduated in true cubic centimetres. With gas-volumetric apparatus this procedure is essential. If the calibration is performed at a temperature of 18°–20°, variations from the true volume resulting from the expansion of the glass are so small for the intervals of temperature through which the laboratory is likely to vary, that they may be neglected.

The vessels are checked by ascertaining the weight of distilled water at a known temperature which they will contain or deliver as the case may be. A large beaker of distilled water is placed in the balance room, and left for some hours till its temperature has become constant. The vessels to be calibrated are thoroughly cleansed by successive treatments with concentrated caustic potash, distilled water, and a warm solution of chromic acid in concentrated sulphuric acid, and then rinsed well with distilled water. The flasks are then dried. A narrow strip of paper is attached vertically to the neck of the litre flask near the mark, the flask placed on one pan of a large balance capable of responding to 0·05 gram, and counterpoised. Weights corresponding with the weight of water which at the temperature of the supply in use will occupy 1000 c.c., are then placed in the pan; the flask is filled nearly to the mark with water, and water is gradually added until flask and weights are in equilibrium. Any water adhering to the inside of the neck of the flask above the mark must be removed by means of filter paper. If the mark on the neck of the flask is thus found to be in error, a pencil mark is made on the strip of paper at the point corresponding with the lower edge of the meniscus, the glass above and below is evenly coated with a thin film of wax, and a horizontal ring is scratched through by means of a needle precisely on a level with the pencil mark. The ring is covered with a small piece of filter paper, which is moistened with hydrofluoric acid, care being taken to remove air-bubbles. After a few minutes the acid is washed off and the wax removed, when a new mark will be found etched into the glass.

In calibrating volumes by determining weights of water, it is necessary to reduce the

weight to vacuum standard, and then divide the result by the density of the water in order to obtain accurately the volume in true cubic centimetres. This calculation can be avoided by making use of the following table :—

$t°$	0°	1°	2°	3°	4°	5°
x	1·19	1·13	1·09	1·07	1·06	1·07
$t°$	6°	7°	8°	9°	10°	11°
x	1·09	1·13	1·18	1·25	1·33	1·43
$t°$	12°	13°	14°	15°	16°	17°
x	1·53	1·65	1·78	1·93	2·09	2·25
$t°$	18°	19°	20°	21°	22°	23°
x	2·43	2·62	2·82	3·03	3·26	3·49
$t°$	24°	25°	26°	27°	28°	29°	30°
x	3·73	3·98	4·24	4·52	4·80	5·08	5·38

x is the quantity to be subtracted from 1000 to obtain the apparent weight (in air, when brass weights are employed) of 1000 c.c. of water at the temperature t. For example, at 18° the apparent weight of 1000 c.c. is 1000 − 2·43 = 997·57 grams.

The litre flask having been graduated to contain, it should now be graduated to deliver. The full flask is carefully emptied and allowed to drain for a definite time—say thirty seconds—again counterpoised with the water adhering to the inside, and again filled with a further 1000 c.c. of water in the manner previously described. The other flasks are graduated in the same way, subtracting only $\frac{1}{2}x$ from 500 grams in the case of the 500 c.c. flask, $\frac{1}{4}x$ from 250 grams for the 250 c.c. flask and so on.

The quantity of liquid which a pipette will deliver depends to some extent on the manner in which it is emptied. A small quantity of liquid always remains in the jet, and this should not be blown out. The best plan is to allow the pipette to empty itself whilst held vertically, and then to let it drain for twenty seconds with the point of the pipette just touching the side of the receiving vessel; but the method of emptying employed in the calibration must be adhered to in its subsequent use.

To test the accuracy with which a pipette has been graduated, it is filled to the mark with distilled water at an observed temperature, the contents delivered into a light, tared, stoppered flask, and accurately weighed. The operation is repeated several times, and from the mean result the true volume is calculated by using the table previously given; for it is clear that $1-\frac{x}{1000}$ denotes the apparent weight of 1 c.c. of water at $t°$, or $1+\frac{x}{1000}$ equals the volume at $t°$ occupied by 1 gram of water weighed in air with brass weights. If the error in graduation is greater than can be allowed, another mark must be made; its position may be found by repeated trials, a strip of paper being pasted along the stem, and the volumes corresponding to various pencil marks being found as above. The new mark is then etched in with hydrofluoric acid.

A convenient method for directly calibrating pipettes is described by Thorpe (Quantitative Analysis). The pipette is suspended from one arm of a balance by means of a clip, so as to hang perpendicularly and pass through a hole in the bottom of the balance case or of a specially constructed table. A suitable clip (Fig. 10) consists of a stout brass wire frame carrying two clips of sheet brass closed by sliding collars. The upper end of the pipette is passed through the lower clip and connected by caoutchouc tubing with a glass stopcock fixed in the upper clip. The other end of the stopcock is provided with a piece of caoutchouc tubing, to which a piece of thermometer tube or a piece of wider glass tube can be attached. The wider glass tube, which serves as a mouthpiece, is first attached to the stopcock, and the pipette is filled with water to a short distance above the mark, and then emptied by the method to be adopted in its subsequent use. It is then counterpoised on the balance with the adhering water inside, the wide tube being replaced by the thermometer tube, and the requisite weights placed on the other pan. The pipette is again filled to a short distance above the mark; the thermometer tube, which is drawn out at one end, is attached again, and the stopcock is opened. Water drops very slowly from the end of the pipette, and it can be arrested the moment the balance is in equilibrium. The level of the water is marked on a piece of paper gummed to the pipette, and a new ring etched with hydrofluoric acid.

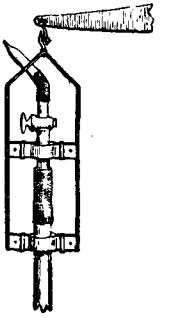


FIG. 10.

The burette is most simply calibrated by the method due to Ostwald with the help of a small pipette of about 2 c.c. capacity, attached to the burette as indicated in Fig. 11. The burette and pipette are filled with water to the zero mark and the mark a respectively, taking care to leave no air bubbles in the tubes. The clip I (or the tap of the burette) is opened and water allowed to run from the burette into the pipette till the level b is reached. The burette reading is then noted, and the pipette emptied to mark a. These operations of filling the pipette, taking a burette reading, and then emptying the pipette, are repeated to the full extent of the burette readings. Suppose, for example, that after twenty-four fillings the burette reading is 49·49 c.c. The burette is now refilled, and exactly this amount of distilled water is run out into a tared flask and

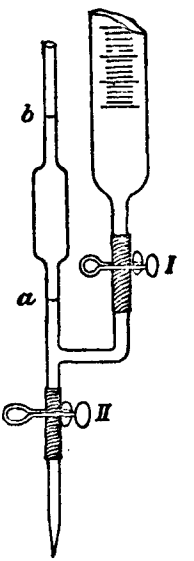


FIG. 11.

weighed, using all the precautions that would be observed in an actual titration. From the table already given the true volume of this water is calculated. Suppose this to be 49·44 c.c. Then the volume of the calibrating pipette must be $\frac{49{\cdot}44}{24} = 2{\cdot}060$ c.c. The differences between the successive burette readings and the successive numbers 2·06, 4·12, 6·18 . . . give at once the burette errors at these intervals, due regard being paid to the sign of the difference. In the example quoted, the correction to be applied for 50 c.c. is obviously −0·05 c.c. (*see* J. Amer. Chem. Soc. 1900, 22, 149; and for a modification of above, J. Amer. Chem. Soc. 1901, 23, 484).

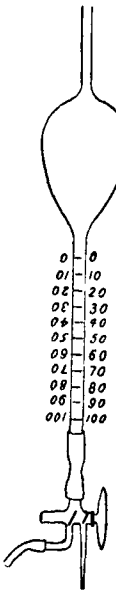


FIG. 12.

A better design for a calibrating pipette is shown in Fig. 12, which also illustrates the Greiner and Friedrich three-way tap (Morse and Blalock, Amer. Chem. J. 1894, 16, 479).

The gas burettes described under *Gas analysis* may be calibrated in much the same way as an ordinary burette, by filling with water or mercury, drawing off aliquot portions and weighing them, the temperature of the liquid being noted and the appropriate correction made for expansion. Any error thus detected must be used as a correction in subsequent readings.

Standard solutions. — These form the basis of all volumetric work, and great care should be exercised in their preparation. When a solution is used only for the estimation of one substance, it may be convenient to adjust its strength so that each c.c. is equivalent to some simple and definite quantity of the substance, say 0·01 gram; but for general purposes the so-called *normal solutions* should be employed. A *normal solution* contains in 1000 c.c. the equivalent in grams of the active substance. A solution of one-tenth this strength is termed a *decinormal* solution, and one of a hundredth a *centinormal* solution. Thus a normal solution of sulphuric acid contains 49·04 grams of real acid per litre, a decinormal solution of iodine contains 12·69 grams of iodine per litre, and each litre of a decinormal solution of potassium permanganate contains 0·8 gram of active oxygen.

Standard solutions are usually made up approximately normal or decinormal as the case may be, and afterwards accurately standardised by titration against a weighed amount of some pure compound. If the solution has been purposely made rather too concentrated, it may then be suitably diluted until exactly normal or decinormal. Since accurate adjustment by dilution is difficult to effect, and in certain cases inadvisable, it is usually better to avoid the process and determine *a factor* by which readings must be multiplied in order to convert them into equivalent readings of a normal or decinormal solution. For example, if 1 c.c. of potassium permanganate solution is found to be capable of oxidising 0·005630 grams of iron, then since the corresponding figure for a decinormal solution is 0·005585, the permanganate is $\frac{5630}{5585}$, or 1·008 times decinormal, and when using it to estimate a substance of equivalent x, each c.s. of permanganate will oxidise $\frac{x}{10000} \times 1{\cdot}008$ grams of substance. When only one or two litres of a standard solution are required, and the pure reagent is at hand, the exact quantity may be weighed out and diluted to the appropriate volume; *e.g.* solutions of silver nitrate and potassium dichromate may be thus prepared.

Measurements.—In measuring out solutions, &c., the vessels must be perfectly dry, which is inconvenient, or must be well drained and then rinsed out with a small quantity of the solution to be measured, which is allowed to run away.

To read correctly the level of the liquid in a burette or pipette requires certain precautions. In the first place, the instrument must be held in a vertical position. Ordinary liquids form a concave surface, or meniscus, and the reading should always be taken from the lowest point of this curve, except in the case of very dark-coloured solutions, when the upper line of the surface must be taken. The meniscus must be properly illuminated, and on a level with the eye, in order to avoid parallax. The best method of avoiding this error is by the use of a burette having the graduation marks carried half-way round the tube. In default of such a burette, use may be made according to Mohr of a piece of card one-half of which is black and the other half white. This is attached to the burette by an indiarubber ring, and is adjusted so that the horizontal edge of the black half, which is lowest, is 2 to 3 mm., *but not more*, below the meniscus. The lower edge of the curve then appears black against the white background. If the card is too low, the reading will be slightly too high. The little clamp and screen designed by Göckel are based on the same principle. Some burettes are provided at the back with a dark vertical line on a milk glass background. When the eye is on a level with the bottom of the meniscus, the dark line appears to be drawn out to two fine points which just touch one another. By means of these devices accurate readings can easily be taken even without using a burette float.

In addition to the errors incident to all analytical processes, another error arises in volumetric analysis, owing to variations in the concentrations of the solutions due to changes of temperature. In the case of $N/10$-solutions this affects the results to the extent of 0·1 p.c. for each 5° variation in temperature. With concentrated solutions, especially those of the acids and alkalis, the error is greater. The coefficients of expansion of certain standard solutions have been determined by A. Schulze (Zeitsch. anal. Chem. 21, 167).

Errors due to changes of temperature may be eliminated by weighing the solutions instead of measuring them. The liquid is contained in a light glass bottle, with a long jet-like neck, and a tubulus at the shoulder which can be closed by the finger, and the flow of liquid thus regulated. The bottle is weighed, the solution

poured gradually from it until the reaction is complete, and the bottle again weighed. The difference between the two weighings gives the quantity of solution used. Convenient weight burettes are described in Chem. News, 1877, 35, 98; J. Amer. Chem. Soc. 1908, 30, 31.

Volumetric methods may be broadly classified as I. Methods of Saturation; II. Methods of Oxidation and Reduction; III. Methods of Precipitation; and examples of the two latter types of processes are indicated below. (For methods of saturation, *v.* ACIDIMETRY AND ALKALIMETRY.)

In the following section the methods for preparing and standardising the more commonly employed solutions are first described, followed by details of the various volumetric estimations for which these solutions may be conveniently employed, alphabetically arranged under the names of the elements that are determined.

PREPARATION OF STANDARD SOLUTIONS.

Potassium permanganate.

Employed as an oxidising agent, usually in dilute sulphuric acid solution, when the permanganate decomposes according to the equation:

$$2KMnO_4+3H_2SO_4 = K_2SO_4+2MnSO_4+3H_2O+5O.$$

The oxidation of ferrous sulphate, for example, is represented in the following manner:—

$$2KMnO_4+10FeSO_4+8H_2SO_4 = K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O$$

and of oxalic acid thus:

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4 = K_2SO_4+2MnSO_4+8H_2O+10CO_2.$$

In order to facilitate calculation, these oxidations are conveniently expressed as a transference of oxygen from one oxide to another, *e.g.*:

$$10FeO+Mn_2O_7 = 5Fe_2O_3+2MnO.$$

The utility of permanganate solution depends upon the facts that such oxidation processes are usually quite easy to effect, the endpoint being readily indicated by the solution acquiring a faint permanent pink tinge, due to the presence of a slight excess of permanganate, which thus acts as its own indicator. Oxidation usually proceeds rapidly at the ordinary temperature, but solutions of oxalic acid must be heated to 60°–80°. It is most essential that a considerable excess of sulphuric acid should be present (about 5 c.c. of concentrated acid per 100 c.c. of solution), since otherwise the solution becomes turbid owing to the separation of manganese dioxide, and the determination is spoilt. The presence of hydrochloric acid in the solution should be avoided, if possible, since it reacts with the permanganate under certain circumstances, particularly in the presence of iron salts. The error that thus arises can be reduced to a negligible amount by adding manganese sulphate to the solution, and titrating very slowly (*see Iron*, p. 211).

Preparation and titration of the solution.—A decinormal solution containing 3·16 grams of the salt per litre of solution is most convenient for general use; it is most readily prepared by grinding the solid repeatedly with small amounts of distilled water in a mortar and decanting the solution into the stock bottle. After a day or two, the solution is filtered through asbestos, and standardised. If kept away from direct sunlight, reducing gases and dust, it retains its titre for a long time; its spontaneous decomposition is largely augmented by the presence of solid dioxide, which explains the necessity for the filtration through asbestos (Amer. Chem. J. 1896, 18, 401).

The solution is best standardised against electrolytic iron, anhydrous sodium oxalate, or by the iodimetric method of Volhard, using a thiosulphate solution which has been recently titrated against pure iodine. (For the latter method, *see Thiosulphate solution*, and for the first, which requires a somewhat complicated apparatus, consult Treadwell-Hall, vol. 2, 81.)

Titration by sodium oxalate.—This method was proposed by Sörensen, and its accuracy has been fully established by various other chemists (Zeitsch. angew. Chem. 1902, 15, 1244; 1904, 17, 230 and 269; 1905, 18, 1520). The pure oxalate, prepared by Kahlbaum according to Sörensen's directions, should be dried at 100° for a few hours before use.

Three or four portions of the oxalate, each weighing about 0·25–0·30 grams, are dissolved in an excess of dilute sulphuric acid; the solutions are warmed to 60°–80°, and titrated with the permanganate solution until a faint, permanent pink colouration is obtained. From the relation $2Na_2C_2O_4 = O_2$, the value of the permanganate solution is calculated for each titration, and the mean of the concordant results adopted as the true value.

Many other methods for standardising permanganate have been proposed, *e.g.* titration against crystalline oxalic acid $H_2C_2O_4,2H_2O$, ammonium oxalate $(NH_4)_2C_2O_4,H_2O$, ferrous sulphate $FeSO_4,7H_2O$, Mohr's salt $FeSO_4.(NH_4)_2SO_4,6H_2O$, &c., which although at times convenient, are less accurate than the methods given. Standardisation against iron wire is not to be recommended, since the small quantities of oxidisable impurities present consume more permanganate than would be required by their own weight of iron, and the error is augmented by making allowance for the actual iron content of the wire (Zeitsch. anal. Chem. 1903, 42, 359; Zeitsch. angew. Chem. 1901, 14, 1233; also Treadwell-Hall, *l.c.*).

It is usual to express the concentration of a permanganate solution in terms of the amount of iron it can oxidise; thus 1 c.c. of *N*/10-$KMnO_4$ = 0·005585 gram Fe.

Potassium dichromate.

A solution of this reagent may replace permanganate in the titration of ferrous salts, with the advantage that it can be used in the presence of either hydrochloric or sulphuric acid. An excess of free acid is essential, the oxidation of ferrous chloride, for example, proceeding according to the equation:

$$K_2Cr_2O_7+6FeCl_2+14HCl = 2KCl+2CrCl_3+6FeCl_3+7H_2O$$

which is essentially:

$$2CrO_3+6FeO = Cr_2O_3+3Fe_2O_3.$$

A decinormal solution obtained by dissolving

$\frac{K_2Cr_2O_7}{60}$ = 4·903 grams of the pure dry recrystallised salt in distilled water and diluting the solution to 1 litre, requires no further standardisation. A stock solution of approximate strength may be standardised against several weighed amounts (1·0–1·4 grams) of pure ferrous ammonium sulphate by a similar procedure to that described under the standardisation of permanganate by sodium oxalate. The titrations, however, are made in cold solution, and the dilute sulphuric acid used should be gently boiled for half an hour to expel dissolved air, and cooled rapidly just before use. Since the green colour of the chromic salt prevents the excess of dichromate from being seen, an external indicator is necessary. Drops of a *dilute* solution of potassium ferricyanide, free from ferrocyanide, are placed on a white plate, and from time to time the end of a glass rod, previously dipped in the titrating flask, is brought into contact with a drop of the ferricyanide. As long as any ferrous salt remains a blue precipitate is produced; the approach of the end is indicated by the decrease in intensity of the blue colouration, and when very near the end about thirty seconds should be allowed for the colour to develop. The end-point is reached when the blue colour ceases to appear. The ferricyanide solution should be prepared only when required by dissolving in water a crystal of the salt which has been rinsed to remove superficial ferrocyanide: the yellow colour of the drops on the white plate should be barely visible; if the ferricyanide is too concentrated, the blue colouration changes through various shades of green into a brown tint.

Iodine, Sodium thiosulphate, and Sodium arsenite.

Decinormal solutions of these reagents are frequently used in conjunction with one another. The reaction between iodine and sodium thiosulphate is essentially:

$$2Na_2S_2O_3+I_2 = Na_2S_4O_6+2NaI$$

although under certain circumstances oxidation to sulphate proceeds to a small extent, even at the ordinary temperature (Pickering). When using decinormal solutions the end-point is readily indicated by the appearance or disappearance of the yellow colour of the iodine, provided the solution undergoing titration is not unduly diluted and is otherwise colourless. The production of a blue colour when free iodine and starch solution are brought together is, however, much more sensitive, and is the method usually employed in ascertaining the end-point.

Preparation of starch solution.—About 1 gram of powdered starch is rubbed into a paste with a little cold water, and slowly added to 200 c.c. of boiling water, the boiling is continued for two or three minutes, the solution cooled, and after some hours the clear liquid is decanted. The solution will only keep for one or two days, unless sterilised, when it is conveniently preserved in small bottles, completely filled and closed by soft rubber stoppers; it will then keep indefinitely. Starch paste prepared from Gastine's formula (5 grams starch, 0·01 gram mercuric iodide, and 1 litre water) retains its sensitiveness for a long time. Addition of 1 c.c. of oil of cassia to a litre of starch liquor is also recommended as a preservative.

Sensitiveness of the iodine-starch reaction.—This depends upon several circumstances. It is necessary to work with cold solutions, preferably neutral or slightly acid; the presence of mineral acid in high concentration greatly impairs the sensitiveness of the reaction, since it hydrolyses the starch. It is essential that a soluble iodide should be present (usually this is potassium iodide) in moderate amount; the best concentration of potassium iodide to employ is about *N*/150, since the sensitiveness of the reaction then reaches a maximum (*see* Zeitsch. anal. Chem. 1902, 41, 485; Amer. J. Sci. 1900, [iv.] 10, 151; J. Amer. Chem. Soc. 1909, 31, 1038).

Good starch solution first yields a pink colouration with iodine, which more iodine develops into the blue colour; starch which produces green tints should be rejected (J. Amer. Chem. Soc. 1908, 30, 31). It frequently happens in titrating arsenious and antimonious oxides with iodine that various tints of red make their appearance instead of the usual blue colouration. This is due to impurity in the starch: in such a case one or two grams of potassium iodide are added, the end-point being ascertained from the development of the yellow colour of the iodine, and then confirmed by the starch (Amer. J. Sci. 1902, [4] 13, 379).

For the *iodine solution* 25 grams of potassium iodide are dissolved in a little water, 12·7 grams of commercial iodine added, and the mixture shaken till the iodine has dissolved; the solution is then filtered through asbestos and diluted to 1 litre. It should be kept in the dark, and protected from dust. For the *thiosulphate solution* the crystalline salt $Na_2S_2O_3$, $5H_2O$ is dissolved in distilled water, using 25 grams per litre, and the solution kept away from direct sunlight for two weeks before it is standardised. It then retains its titre for months. For the *sodium arsenite*, 4·948 grams of resublimed arsenious oxide are dissolved in a little warm sodium hydroxide free from iron, the solution rinsed into a litre flask, and made just acid to phenolphthaleïn with dilute sulphuric acid. A filtered solution of 20 grams of sodium bicarbonate in 500 c.c. of water is added, and if the mixture reacts alkaline to the phenolphthaleïn, sulphuric acid added till the pink colour disappears. This solution, when diluted to 1 litre and thoroughly mixed, is strictly decinormal, and keeps indefinitely. A measured quantity of the *N*/10-arsenite solution is delivered into an Erlenmeyer flask, and the iodine solution run in from the burette until present in slight excess, starch paste being added nearly at the finish of the titration (*see* remarks on starch above). The reaction

$$As_2O_3+2I_2+2H_2O \rightleftharpoons As_2O_5+4HI$$

proceeds to completion in the sense of the upper arrow in neutral solution, a condition secured by the presence of the bicarbonate, which neutralises the hydriodic acid produced. Since the solution should be saturated with carbon dioxide, it is advisable to stopper the flask except when actually introducing the iodine (J. Amer. Chem. Soc. 1908, 30, 31).

The iodine being standardised, the thio-

sulphate can be directly titrated against it, preferably by running the iodine into a measured volume of thiosulphate.

Many alternative methods have been proposed for standardising iodine and thiosulphate solutions. The latter may be titrated against pure iodine: 0·5 gram of pure iodine and 0·1 gram of potassium iodide are powdered and mixed together in a porcelain dish, and heated on a sand-bath till vapour is copiously evolved; the dish is then covered with a dry watch-glass, and the greater part of the iodine sublimed on to it. The watch-glass is covered with a second accurately fitting glass and the whole weighed, the weight of the glasses having been previously found. The whole is gently placed in a solution of 1 gram of potassium iodide in 10 c.c. of water, and after a few seconds the solution is diluted to 100 c.c. and titrated with the thiosulphate.

The thiosulphate may also be standardised against permanganate, itself verified by reference to sodium oxalate. One or two grams of potassium iodide are dissolved in water, acidified with 5 c.c. of hydrochloric acid (1 : 5) and 25 c.c. of standard permanganate added. The iodine, which is quantitatively liberated:

$$Mn_2O_7 + 10HI = 2MnO + 5H_2O + 5I_2$$

is then titrated with the thiosulphate, after diluting the solution to 100 c.c. By the reverse process of calculation, a permanganate solution may be standardised against a thiosulphate solution that has been verified by either of the preceding methods (*see Standardisation of permanganate; cf.* Annalen, 1897, 198, 333; Zeitsch. angew. Chem. 1904, 17, 815; Ann. Chim. Anal. 1904, 9, 365; Zeitsch. anorg. Chem. 1906, 49, 277).

(For the use of potassium dichromate in this connection, *see Volumetric estimation of chromium;* Zeitsch. anorg. Chem. 1899, 19, 427; 1906, 49, 277. *See* also *Copper* under *Volumetric estimations.* For a gravimetric method for standardising iodine solution, consult Amer. J. Sci. 1909, (iv.) 28, 33.)

Titanous chloride.

This reagent, introduced into volumetric analysis by Knecht (J. Soc. Dyers and Colourists, 19, No. 6; Ber. 1907, 40, 3819), is a powerful reducing agent. For example, a hydrochloric acid solution of ferric chloride is quickly and quantitatively reduced in the cold, according to the equation:

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$

and the end-point is reached when a drop of the liquid ceases to produce a red colouration with potassium thiocyanate. Chromic acid and cupric salts may be similarly estimated, and also a large number of organic dyes.

Fifty c.c. of the commercial 20 p.c. solution of titanous chloride, which usually contains a little iron, are mixed with an equal volume of concentrated hydrochloric acid, boiled for several minutes, and diluted to 1 litre with air-free water. The solution must be kept protected from the air; a convenient method is figured in Sutton's Volumetric Analysis (9th ed.), p. 224.

The concentration of the solution is fixed by titrating against a known quantity of either ferric salt or potassium dichromate. In the former case 35 grams of pure ferrous ammonium sulphate are dissolved in dilute sulphuric acid and the solution diluted to 1 litre; 25 c.c. are then exactly oxidised with dilute permanganate, and the resulting ferric sulphate titrated with the titanous chloride until a drop of the solution no longer gives a red colour with potassium thiocyanate. Instead of using this 'spot-out' method, 10–20 c.c. of 10 p.c. potassium thiocyanate may be added to the ferric solution. If the standardisation be effected with potassium dichromate, addition of the indicator to the solution itself is inadmissible. Nearly all the titanous chloride necessary, may, however, be added at once, since the colour changes, through orange to green and then violet, afford an indication of the end-point. Drops of solution are removed for testing when the green colour has just disappeared (J. Soc. Chem. Ind. 1908, 27, 673).

Pure ferric alum, the preparation of which is described by De Koninck (Bull. Soc. chim. Belg. 1909, 23, 222), might also be employed for this standardisation.

For a number of estimations it is necessary to employ titanous sulphate instead of the chloride.

Stannous chloride.

This reagent has long been employed as a reducing agent, but the closely allied and more powerfully reducing titanous salts appear to be displacing it. Ferric salts are easily reduced in hot acid solution:

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

Iodine in cold acid solution oxidises it quantitatively:

$$2SnCl_2 + 2I_2 = SnI_4 + SnCl_4.$$

Ten grams of pure tin in thin pieces are heated with 200 c.c. of concentrated hydrochloric acid in a platinum dish until dissolved: or a glass flask may be used with a piece of platinum foil touching the tin to promote its speedy solution. The solution is diluted to 1 litre, and preserved out of contact with the air.

The solution is best standardised by that process for which it is afterwards to be employed, *e.g.* if required for iron estimations, by titration against a known amount of ferric chloride. The latter may be obtained by dissolving 10·03 grams of bright iron wire (99·7 p.c. iron) in hydrochloric acid, oxidising with potassium chlorate, expelling the excess of chlorine by boiling, and diluting the solution to 1 litre; 25 c.c. are conveniently used for titrating the above solution.

Several methods have been proposed for determining the end-point. The iron solution containing 20–40 c.c. of concentrated hydrochloric acid in a volume of 125 c.c. may be titrated nearly at the boiling-point, 15 c.c. of indicator solution (34 grams $HgCl_2$ + 0·05 gram Pt as chloride per litre) being added. The end-point is reached when a dark-cloud of finely divided mercury and platinum is produced (Amer. Chem. J. 1893, 15, 360). Or a drop of the solution may be mixed with ammonium molybdate on a white plate; the slightest trace of stannous salt causes a blue colouration. An alternative is to add a slight

excess of stannous chloride, and titrate back the cold solution with iodine.

(For the standardisation by means of iodine, *see Volumetric estimation of tin.*)

Silver nitrate, Sodium chloride, and Ammonium thiocyanate.

These precipitation reagents, which are conveniently made of decinormal strength, are of great service for the volumetric estimation of silver, copper, mercury, the halogen acids, cyanides, and thiocyanates.

Silver nitrate is used either in neutral or in nitric acid solution. In the first case potassium chromate is employed as indicator when halogens are being estimated (Mohr's method). Silver chromate is decomposed by solutions of halogen salts forming silver halide and metallic chromate; consequently, silver chromate cannot permanently exist in the solution until all the halogen has been precipitated. The first drop of silver nitrate in excess then produces a permanent precipitate of silver chromate, which gives a faint red tint to the previously pale-yellow liquid. This colour change is more readily observed in monochromatic light (from a powerful sodium flame). One or two drops of a 10 p.c. solution of potassium chromate are added to the solution, which should not be unduly diluted. Silver chromate is soluble in mineral acids or ammonia; hence the necessity for working in neutral solution. An alkaline solution may be acidified with dilute nitric acid, and then neutralised with powdered calcium carbonate. Barium must be absent from the solution, since it precipitates the indicator; it may be removed with sodium sulphate.

In the presence of nitric acid, silver nitrate and ammonium thiocyanate solutions are used in conjunction (Volhard's method, Annalen, 1878, 190, 47). The addition of thiocyanate to a nitric acid solution containing silver causes the precipitation of white silver thiocyanate, and the end-point is indicated by the red colouration produced by the interaction of the first drop of thiocyanate in excess with a ferric salt previously introduced into the solution. The thiocyanate should always be added to the silver solution. The ferric indicator is prepared by adding nitric acid (4 : 1 boiled to expel nitrous acid) to a saturated solution of iron alum until colourless; 5–10 c.c. are used in the titration.

Standard sodium chloride solution is used for the estimation of silver by the very exact method originally due to Gay-Lussac. (For a description of the method, *v.* ASSAYING.)

Decinormal silver nitrate is obtained by dissolving 16·99 grams of the pure dry recrystallised silver nitrate in water and diluting the solution to 1 litre. If it is to be used in conjunction with the thiocyanate, this solution may also be prepared by dissolving 10·788 grams of pure silver in a slight excess of nitric acid, boiling till nitrous acid is expelled, and diluting to 1 litre.

The thiocyanate is prepared approximately decinormal by dissolving the salt in distilled water (8 grams per litre), and is standardised against the silver nitrate solution, 25 c.c. of which are diluted to 100 c.c. and titrated as described above.

VOLUMETRIC ESTIMATIONS.

Aluminium. *Iodimetrically.* The neutral solution is boiled with excess of potassium iodide and potassium iodate for twenty minutes in a stream of hydrogen; the iodine evolved, and collected in potassium iodide, together with that which remains in the distilling flask, is titrated with $N/10$-thiosulphate (Amer. J. Sci. 1905, 20, 181; Zeitsch. anorg. Chem. 1907, 52, 286):

$$Al_2(SO_4)_3+5KI+KIO_3+3H_2O = 2Al(OH)_3+3K_2SO_4+3I_2.$$

Antimony. ANTIMONIOUS SOLUTIONS. (*a*) *Iodimetrically.* One or two grams of Rochelle salt are added, the solution made alkaline with sodium bicarbonate, and titrated with $N/10$-iodine. $I_2 = Sb$ (*v.* ARSENIC).

(*b*) *By oxidation.* The hot hydrochloric acid solution (above 60°) is titrated with $N/10$-potassium bromate, which has been standardised against a known amount of pure antimony—

$$3SbCl_3+KBrO_3+6HCl=3SbCl_5+KBr+3H_2O.$$

The end-point is indicated by the bleaching of a few drops of methyl orange added to the hot solution (Chem. Zeit. 1903, 27, 749; J. Soc. Chem. Ind. 1906, 25, 1181; Chem. News, 1907, 95, 49).

(*c*) *By oxidation.* The cold solution, freely acidified with hydrochloric acid, is titrated with $N/10$-permanganate (Zeitsch. angew. Chem. 1901, 14, 1179; J. Amer. Chem. Soc. 1907, 29, 66).

ANTIMONIC SOLUTIONS. (*a*) *By reduction* to the tervalent state, and estimation by one of the foregoing processes. Reduction may be accomplished: (i.) by boiling the hydrochloric acid solution with sodium sulphite or sulphurous acid (Zeitsch. angew. Chem. 1888, 155); according to Rohmer, the reduction is not quantitative unless a gram of potassium bromide is added (Ber. 1901, 34, 1565); (ii.) by boiling the sulphuric acid solution (100 c.c. containing 5 c.c. of concentrated acid and 4 grams of Rochelle salt) with 1·0–1·5 grams of potassium iodide till nearly all the iodine is expelled, exactly bleaching the remainder with dilute sulphurous acid, diluting, rapidly cooling, and neutralising. The solution is then titrated in bicarbonate solution with $N/10$-iodine (Amer. J. Sci. 1892, 42, 213).

(*b*) *Iodimetrically.* The cold solution containing 20–25 c.c. of hydrochloric acid in a volume of 100 c.c., is mixed with 0·5–1·0 gram of potassium iodide and the liberated iodine titrated with $N/10$-thiosulphate. $I_2 = Sb$ (Zeitsch. anorg. Chem. 1908, 58, 202; cf. *ibid.* 1903, 37, 337).

Arsenic. ARSENIOUS SOLUTIONS. *Iodimetrically.* The solution, containing sodium bicarbonate in excess, is titrated with $N/10$-iodine as described under the standardisation of iodine solution. The bicarbonate may with advantage be replaced by disodium hydrogen phosphate (J. Amer. Chem. Soc. 1908, 30, 31).

ARSENIC SOLUTIONS. (*a*) *By reduction* with hydriodic acid as described under *Antimony*, and subsequent titration with iodine; no Rochelle salt is necessary (Amer. J. Sci. 1900, 10, 151). Reduction may also be effected by heating the sulphuric acid solution with sulphurous acid in a stoppered bottle for an hour, diluting and boiling down to half the volume to expel excess

of sulphurous acid (Zeitsch. anal. Chem. 1883, 22, 378; Chem. News, 1886, 53, 221).

(*b*) *By precipitation.* The neutral or acetic acid solution is precipitated with excess of silver nitrate, and the precipitated silver arsenate collected, washed, dissolved in nitric acid, and the silver titrated with $N/10$-thiocyanate. $3Ag=As$.

(*c*) *Iodimetrically* (Zeitsch. anal. Chem. 1906, 45, 596; compare Amer. J. Sci. 1900, 10, 151). (*See* also Zeitsch. anorg. Chem. 1909, 62, 123, for a method suitable for small quantities of arsenic.)

Barium. *Iodimetrically.* Excess of potassium iodate is added to the faintly ammoniacal solution, the precipitated iodate washed with ammonia and then with alcohol, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated with $N/10$-thiosulphate. $6I_2=Ba$ (J. Amer. Chem. Soc. 1909, 31, 43).

Bismuth. (*a*) *Iodimetrically.* The solution, as free as possible from mineral acids, is mixed with excess of $N/2$-potassium chromate, shaken for 10 minutes, diluted to a known volume, and the chromate in an aliquot part of the filtrate from the bismuthyl chromate $Bi_2O_3{\cdot}2CrO_3$ is titrated iodimetrically (Zeitsch. anorg. Chem. 1902, 32, 362; Zeitsch. anal. Chem. 1907, 46, 223).

(*b*) As *bismuth ammonium molybdate* (J. Amer. Chem. Soc. 1903, 25, 907).

Boron. (*a*) *v.* ACIDIMETRY AND ALKALIMETRY.

(*b*) *Iodimetrically.* The reaction

$$5KI+KIO_3+6HBO_2=3I_2+3H_2O+6KBO_2$$

is quantitative in a solution saturated with mannitol (*v.* Amer. J. Sci. 1899, 8, 127).

Bromine *v. Halogens.*

Calcium. *By oxidation.* The oxalate, precipitated from a hot slightly ammoniacal solution (*see Gravimetric methods*), is washed with warm water till free from ammonium oxalate, decomposed with hot dilute sulphuric acid, and the oxalic acid titrated with $N/10$-permanganate. The precipitate may also be dissolved in dilute hydrochloric acid, 0·5 gram of manganese sulphate added, and the solution titrated with permanganate (*v.* Amer. Chem. J. 1905, 33, 500).

Carbon. CARBON DIOXIDE. *v.* ACIDIMETRY and ALKALIMETRY, and *Gas analysis.*

CYANOGEN ACIDS. CYANATES. The cold, dilute solution is exactly neutralised with $N/10$-hydrochloric acid (using methyl orange or congo red as indicator), excess of acid is added, the solution boiled for ten minutes, cooled and titrated back $N/10$-sodium hydroxide. Excess of $N/10$-sodium hydroxide is then added, the solution boiled to expel ammonia, and titrated back with $N/10$-hydrochloric acid. From these data two values for the cyanate can be calculated, which serve to check one another (Chem. News, 1906, 93, 5; compare Zeitsch. angew. Chem. 1901, 24, 585; J. Soc. Chem. Ind. 1904, 23, 244).

$$KCNO+2HCl+H_2O = KCl+NH_4Cl+CO_2.$$

CYANIDES. (*a*) *By precipitation.* (i.) Excess of $N/10$-silver nitrate is added to the neutral cyanide solution, and then a little nitric acid. The excess of silver is titrated with $N/10$-thiocyanate after filtering off the silver cyanide. (ii.) The slightly alkaline solution is titrated with $N/10$-silver nitrate with constant stirring till a permanent turbidity is produced (Liebig, Annalen, 1851, 77, 102). This marks the end of the reaction:

$$2KCN+AgNO_3=KNO_3+KAg(CN)_2.$$

The end-point is best observed by adding 5–10 drops of 20 p.c. potassium iodide as an indicator. A permanent yellow turbidity, due to silver iodide, is produced as soon as the above reaction is completed (Ann. Chim. Phys. 1895, (vii.) 6, 381).

(*b*) See *Ferrocyanides* (*b*).

FERRICYANIDES. (*a*) The salt is reduced to ferrocyanide by boiling with sodium hydroxide and ferrous sulphate and the filtered solution strongly acidified with sulphuric acid and titrated with $N/10$-permanganate (*v. Ferrocyanides*). Reduction may also be effected by boiling with sodium peroxide (Arch. Pharm. 232, 226).

(*b*) *Iodimetrically.* The neutral solution (50 c.c.) is mixed with 3 grams of potassium iodide and 1·5 grams of zinc sulphate, the mixture well shaken, and the iodine titrated with $N/10$-thiosulphate. $2K_3Fe(CN)_6=I_2$ (Zeitsch. anorg. Chem. 1910, 67, 418; compare *ibid.* 67, 322).

FERROCYANIDES. (*a*) *By oxidation.* The solution is strongly acidified with sulphuric acid and titrated with $N/10$-permanganate till the colour changes from yellowish-green to yellowish-red. If any difficulty is experienced in determining the end-point, a drop of the solution may be mixed with dilute ferric chloride. A blue colour will develop whilst any ferrocyanide remains (de Haen, Annalen, 1854, 90, 160; compare Zeitsch. anorg. Chem. 1910, 67, 418).

An excess of permanganate may also be added, the excess being determined iodimetrically. (For details, consult Zeitsch. anorg. Chem. 1910, 67, 322.)

(*b*) *By conversion into hydrocyanic acid.* The ferrocyanide solution is boiled for five minutes with 10 c.c. of N-sodium hydroxide and 15 c.c. of $3N$-magnesium chloride, 100 c.c. of boiling $N/10$-mercuric chloride are then added, and the boiling continued for ten minutes. The mercuric cyanide produced is distilled for thirty minutes with 30 c.c. of $3N$-sulphuric acid, the prussic acid collected in 25 c.c. of N-sodium hydroxide, a little potassium iodide added, and the cyanide titrated with $N/10$-silver nitrate (Feld, Chem. Zentr. 1903, ii. 1398; Analyst, 1908, 33, 261; 1910, 35, 295).

THIOCYANATES. (*a*) *By precipitation.* As in standardising ammonium thiocyanate solution; the thiocyanate must be added to the silver nitrate, and not *vice versâ*, since nitric acid decomposes thiocyanates.

(*b*) *By oxidation.* The thiocyanate is titrated in concentrated hydrochloric acid solution with potassium iodate, in a stoppered bottle, with vigorous shaking. The end-point is reached when 5 c.c. of chloroform previously introduced are no longer coloured by iodine (J. Amer. Chem. Soc. 1908, 30, 760); *e.g.*

$$4CuCNS+7KIO_3+14HCl = 4CuSO_4+7KCl+7ICl+4HCl+5H_2O.$$

Oxidation in dilute sulphuric acid solution with permanganate is untrustworthy.

Cerium. (*a*) *Iodimetrically.* Ceric oxide is warmed with concentrated hydrochloric acid and potassium iodide in a stoppered bottle till complete solution is effected. The liberated

iodine is then titrated with $N/10$-thiosulphate (Bunsen, Annalen, 1858, 105, 49; also Amer. J. Sci. 1899, 8, 451).

$$2CeO_2+8HCl+2KI=2CeCl_3+2KCl+I_2+4H_2O$$

(*b*) *By oxidation.* The washed oxalate is suspended in hot dilute sulphuric acid and titrated with $N/10$-permanganate (*v. Calcium*: Zeitsch. anal. Chem. 1880, 19, 194; Amer. J. Sci. 1899, 8, 457).

(*c*) *By reduction.* The cerium is oxidised with sodium bismuthate in boiling sulphuric acid solution to ceric sulphate and the filtered solution reduced by a slight excess of ferrous sulphate, the excess being titrated with $N/10$-permanganate. Other rare earth metals do not interfere (J. Amer. Chem. Soc. 1909, 31, 523; 1910, 32, 642; compare Compt. rend. 1899, 128, 101; Ber. 1900, 33, 1924; Ber. 1903, 36, 282).

(*d*) *Other methods* (Zeitsch. anorg. Chem. 1907, 54, 104; 1908, 59, 71).

Chlorine *v. Halogens.*

Chromium. The chromium should be in the form of chromate.

(*a*) *Iodimetrically.* The chromate solution is acidified with hydrochloric acid (5 c.c. of concentrated acid per 100 c.c. solution), 1 or 2 grams of potassium iodide added, and the covered solution allowed to stand for 15 to 20 minutes. It is then diluted to 400–500 c.c. and the liberated iodine titrated with $N/10$-thiosulphate. $3I_2=2Cr$. A known dichromate solution can in this way be used to standardise sodium thiosulphate (J. pr. Chem. 1868, 103, 362; Zeitsch. anorg. Chem. 1899, 19, 427; 1906, 49, 277; Zeitsch. angew. Chem. 1900, 1147).

(*b*) *By reduction* (i.) with ferrous ammonium sulphate, of which a slight excess is added to the chromate solution containing sulphuric or hydrochloric acid, the excess of ferrous salt being then titrated with $N/10$-dichromate; (ii.) with titanous chloride (*v. Preparation of standard solutions*; J. Soc. Chem. Ind. 1908, 27, 673); (iii.) with arsenious oxide (Amer. J. Sci. 1896, 1, 35).

Chromium in chrome steel. Three grams of alloy are dissolved in 35 c.c. of concentrated hydrochloric acid, and the excess evaporated; 150 c.c. of strong nitric acid are added, the boiling continued till no more brown fumes are evolved, when all chlorine has been expelled. The chromium is then oxidised by adding 10 grams of potassium chlorate, and the solution boiled down to 40 c.c. to decompose excess of chlorate; 100 c.c. of water are added, and one or two drops of hydrochloric acid, to dissolve separated manganese dioxide. The chromate solution is boiled to expel chlorine, cooled and titrated according to method (*b*) (i.) above. (For other methods, *see* J. Amer. Chem. Soc. 1905, 27, 1550; 1908, 30, 1116; J. Soc. Chem. Ind. 1907, 26, 1010; Chem. News, 1904, 90, 320; 91, 3; also *Manganese* and *Vanadium* (*v. infra*).)

Chromium in chromite. The valuation of this, the only important ore of chromium, is usually effected by a volumetric method; the finely powdered ore is fused with sodium peroxide in a nickel crucible, and the chromate in the aqueous extract estimated as described above, after boiling for ten minutes to decompose excess of peroxide (*v.* J. Soc. Chem. Ind. 1896, 15, 155, 436; Chem. Zeit. 1897, 21, 3; Bull. Soc. Chim. 1909, 5, 1133; Chem. News, 1896, 73, 1).

Cobalt. (*a*) *Iodimetrically.* The solution is mixed with hydrogen peroxide, and then with sodium hydroxide, when the cobalt is precipitated as sesquioxide Co_2O_3, whilst nickel is simply precipitated as green hydroxide. After boiling for a minute, the black ppt. is dissolved in hydrochloric acid and potassium iodide, and the iodine titrated with $N/10$-thiosulphate (Chem. News, 1900, 82, 66, 73; 1903, 88, 184).

(*b*) *By precipitation* with ferrocyanide, as described under *Nickel* (*b*).

Columbium. *By reduction and subsequent oxidation* (*v.* Zeitsch. anorg. Chem. 1909, 62, 383).

Copper. (*a*) *Iodimetrically.* The solution of cupric salt preferably neutral or containing acetic acid, is diluted to 100 c.c., 5 grams of potassium iodide are added, and the liberated iodine titrated with $N/10$-thiosulphate, using starch paste as indicator. If more than 25 c.c. of thiosulphate are required, 2–3 grams more potassium iodide should be added (Amer. J. Sci. 1907, 24, 65; compare J. Amer. Chem. Soc. 1902, 24, 1082; 1905, 27, 1224; see also *Methods of separation*).

$$2CuSO_4+4KI=2K_2SO_4+I_2+Cu_2I_2.$$

(*b*) *By titration with potassium cyanide* (*Steinbeck's process*). The ammoniacal copper solution is titrated with potassium cyanide until colourless (*v.* Chem. News, 1897, 76, 189; *Methods of separation*; and the article COPPER).

(*c*) *By precipitation as thiocyanate* and estimation of the precipitate by potassium iodate in hydrochloric acid solution (*v. Thiocyanates*; and J. Amer. Chem. Soc. 1908, 30, 760).

(*d*) *By oxidation.* The oxalate is precipitated in a nitric acid solution by adding excess of ammonium oxalate, washed and titrated with $N/10$-permanganate (Amer. J. Sci. 1909, 27, 448).

(*e*) *By reduction* to cuprous salt. To the sulphuric or hydrochloric acid solution, 10–20 c.c. of 10 p.c. potassium thiocyanate and a little ferrous salt are added, when a deep red colouration is produced, since ferrous salts in acid solution are partly oxidised by cupric salts. The cold solution is titrated with titanous chloride until the red colouration is destroyed (Chem. Soc. Trans. 1906, 89, 1491). Or a slight excess of titanous chloride may be added, and titrated back with standard ferric alum.

Fluorine. *Acidimetrically.* The fluoride is mixed with ten times its weight of finely powdered and ignited quartz, and decomposed by warming with concentrated sulphuric acid; the silicon fluoride evolved passes through a dry U-tube filled with glass beads and immersed in cold water, in order to remove sulphuric acid, and is then absorbed in 50 p.c. alcoholic potassium chloride, which precipitates silicic acid and potassium silicofluoride, leaving hydrochloric acid in the solution :—

$$3SiF_4+2H_2O=2H_2SiF_6+SiO_2$$
$$H_2SiF_6+2KCl=K_2SiF_6+2HCl.$$

The hydrochloric acid is titrated with $N/5$-sodium hydroxide, using lacmoid as indicator. $2HCl=3F_2$. (For full experimental details, which are absolutely essential in order to obtain

accurate results, consult Chem. News, 1879, 39, 179; Amer. J. Sci. 1906, 22, 329; or Low's Technical Methods of Ore Analysis.)

Gold. *Iodimetrically.* The auric solution is treated with potassium iodide in more than sufficient quantity to dissolve the aurous iodide first precipitated, and the iodine liberated is estimated with standard thiosulphate (Amer. J. Sci. 1899, 8, 261; compare Zeitsch. anorg. Chem. 1899, 19, 63).

Halogens. This term is restricted in this connection to chlorine, bromine, and iodine, fluorine being treated separately, since its analytical reactions are quite different.

ESTIMATION OF HALOGENS. *Iodine* is estimated by solution in potassium iodide and titration with $N/10$-thiosulphate, using starch paste as indicator (*v. Preparation of standard solutions*, p. 205). *Bromine* and *chlorine* are absorbed in potassium iodide solution, setting free an equivalent quantity of iodine, which is titrated with $N/10$-thiosulphate.

A large number of substances, *e.g.* peroxides, chlorates, chromates, &c., may be readily determined indirectly by distillation with concentrated hydrochloric acid, the available oxygen of the compound setting free its equivalent of chlorine, which is absorbed in potassium iodide, and the liberated iodine titrated with $N/10$-thiosulphate. It is very desirable to exclude air in the process of distillation, since it liberates iodine from the hydrogen iodide set free in the receiver, by the hydrogen chloride distilling over during the experiment. The apparatus devised by Bunsen, the originator of this analytical method, is shown in Fig. 13, *b*. The

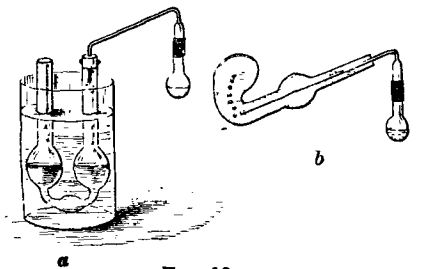


FIG. 13.

small flask (50 c.c.) and the delivery tube are ground at their junction to fit, and the joint made with caoutchouc tubing; a ground-glass joint is better, a spring holding the two parts tightly together. The mixture is rapidly boiled, the chlorine passing into potassium iodide contained in the retort, the size of which must be suitably chosen to prevent overflowing. A different receiving vessel is shown in Fig. 13, *a*. It is very convenient to perform such distillations in a current of carbon dioxide or other inert gas, and various designs of apparatus for such a purpose are given in Amer. J. Sci. 1898, 6, 168; Chem. News, 1899, 79, 85; Chem. Soc. Trans. 1892, 61, 87; Zeitsch. angew. Chem. 1890, 477.

The apparatus shown in Fig. 14 (Analyst, 1908, 33, 117) admits of the gradual introduction of a liquid reagent during distillation in carbon dioxide, steam, or any other gas or vapour. Contamination of the reagents with cork or indiarubber derived from stoppers, &c., is avoided by fitting the condenser and the dropping

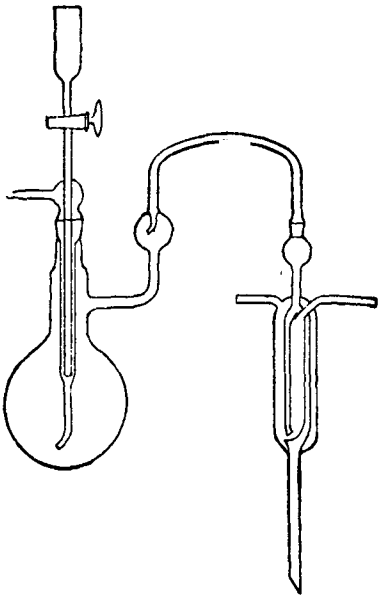


FIG. 14.

funnel to the distilling flask by ground-glass joints.

ESTIMATION OF HALOGENS IN HALIDE SALTS. *By precipitation.* (i.) *Mohr's method.* The neutral solution is titrated with $N/10$-silver nitrate in the presence of a few drops of potassium chromate as indicator (*v. Preparation of standard solutions*, p. 206). It is advisable to perform a blank experiment under identical conditions, to allow for the silver nitrate necessary to bring out the reddish colouration. (ii.) *Volhard's method.* The nitric acid solution of the halide is precipitated by adding a slight excess of $N/10$-silver nitrate, the excess being then titrated with $N/10$-ammonium thiocyanate. Silver chloride must be filtered off before the latter titration is performed, since it reacts with the thiocyanate (J. Amer. Chem. Soc. 1907, 29, 269; compare Zeitsch. anorg. Chem. 1909, 63, 330); but silver bromide and iodide do not interfere. It is advisable to titrate iodide in a stoppered bottle with vigorous shaking when adding both the silver solution and the thiocyanate, to minimise error due to occlusion. It is more accurate to weigh out a very slight excess of pure silver, dissolve it in nitric acid (carefully expelling nitrous acid, which interferes with the indicator), and add to the halide solution than to measure out $N/10$-silver nitrate. After vigorous shaking, the excess of silver is then titrated with a dilute thiocyanate solution (1 c.c. = 1 milligram Ag).

IODIDES. *Iodimetrically.* (i.) A slight excess of potassium iodate is added, and the solution acidified with dilute sulphuric acid. The liberated iodine is extracted with chloroform, carbon disulphide or toluene, and titrated with $N/10$-thiosulphate. A weaker acid than sulphuric acid may be employed, *e.g.* acetic or

tartaric acid. Five-sixths of the iodine found was originally present as iodide (Chem. Zeit. 1904, 28, 1191; Amer. J. Sci. 1897, 3, 293; J. pharm. Chim. 1902, 16, 207; J. Amer. Chem. Soc. 1903, 25, 1138). This method is available in the presence of bromide and chloride, if acetic acid be employed. (ii.) The solution, containing the iodide, 2 grams of pure potassium arsenate, and 10 c.c. of concentrated sulphuric acid, is boiled down from a volume of 100 c.c. to 35–40 c.c., when all the iodine is expelled. The arsenious salt in solution is then titrated with N/10-iodine (Amer. J. Sci. 1890, 39, 188). As $=I_2$. In the presence of chloride the results are a little low; bromide causes them to be slightly high. (iii.) (*v.* Chem. Soc. Trans. 1885, 47, 471.)

ESTIMATIONS OF HALOGENS IN OXYHALOGEN COMPOUNDS. (*a*) *By reduction* to a halide salt and determination of the latter. *Iodates* are reduced by adding sulphurous acid to the sulphuric acid solution of the iodate till the separated iodine is redissolved; an excess of N/10-silver nitrate is added to precipitate the iodide, the mixture boiled with excess of nitric acid, and finally the excess of silver titrated with N/10-thiocyanate. *Bromates and chlorates* are reduced by adding an excess of iron filings to the sulphuric acid solution; after an hour, excess of N/10-silver nitrate is added, the mixture boiled with nitric acid to oxidise the ferrous salt, and the excess of silver titrated (Amer. Chem. J. 1904, 32, 242).

(*b*) *By reduction* to a halide salt and estimation of the reducing agent used up in the process. With *chlorates and bromates*, the sulphuric acid solution is boiled for ten minutes with excess of standard ferrous sulphate in an atmosphere of carbon dioxide, the solution cooled, manganese sulphate added and the unchanged ferrous salt titrated with N/10-$KMnO_4$. $6Fe = ClO_3$ or BrO_3 (Zeitsch. anorg. Chem. 1904, 38, 110). *Bromates* may also be reduced with arsenious oxide (Amer. J. Sci. 1902, 14, 285). *Chlorates* are reduced by adding an excess of N/10-titanous sulphate, and after three minutes, titrating back with ferric alum (J. Soc. Chem. Ind. 1908, 27, 434).

(*c*) *Iodimetrically. Chlorates.* (i.) By distillation with concentrated hydrochloric acid. $ClO_3 = 3I_2$ (*Bunsen's method; v. Estimation of halogens;* Chem. Soc. Trans. 1892, 61, 87). (ii.) By reduction with concentrated hydrochloric acid and potassium bromide (Chem. Zeit. 1901, 25, 727), or with potassium iodide and dilute sulphuric acid in presence of vanadyl sulphate (Zeitsch. anal. Chem. 1907, 46, 521). (For other methods, *see* Amer. J. Sci. 1891, 42, 220; J. Amer. Chem. Soc. 1903, 25, 756; Zeitsch. anal. Chem. 1907, 46, 308.)

Hypochlorites. A slight excess of N/10-sodium arsenite is added and the excess titrated with N/10-iodine, or the hypochlorite is directly titrated with the arsenite till a drop of the solution ceases to colour starch-potassium iodide paper blue. As $= ClO$ (*Penot's method*; compare Chem. Zeit. 1904, 28, 59).

Perchlorates. The concentrated solution is boiled with a large excess of titanous sulphate, the excess oxidised with permanganate, and the chloride produced is titrated as usual (Zeitsch. anorg. Chem. 1909, 62, 108; Chem. Zeit. 1909, 33, 759).

Bromates. The substance is digested at 100° with potassium iodide and concentrated hydrochloric acid in a stoppered bottle, and the liberated iodine titrated with thiosulphate. $BrO_3 = 3I_2$ (compare Zeitsch. anorg. Chem. 1899, 19, 427).

Iodates. These are simply added to a slight excess of potassium iodide solution, acidified with sulphuric or hydrochloric acid, and the liberated iodine titrated. $IO_3 = 3I_2$.

ESTIMATIONS INVOLVING MIXTURES OF THE FOREGOING HALIDE SALTS.

Chloride, Hypochlorite and Chlorate. The solution is titrated with N/10-sodium arsenite by Penot's method for the *hypochlorite*; the *chlorate* is then estimated in the solution, after acidifying with sulphuric acid, by reduction with standard ferrous sulphate, and the total chlorine then titrated by Volhard's method (Compt. rend. 1896, 122, 449; cf. J. Amer. Chem. Soc. 1909, 31, 525, 1273).

Chloride, Chlorate and Perchlorate. Chloride is titrated in one portion of the solution by Volhard's method, and in another portion after reducing the chlorate with ferrous sulphate. For *perchlorate* the dry substance, mixed with five times its weight of pure quartz sand and covered with a layer of the same 2 cm. deep, is fused in a platinum crucible for half an hour, cooled, extracted with water, and the total chloride estimated (Compt. rend. 1896, 122, 452).

Chloride and Iodide. The *total halogen* is titrated by a suitable method in one portion of solution, and the *chlorine* in another portion after removing iodine by one of the following methods (Amer. J. Sci. 1890, 39, 293). (i.) To the neutral solution (400 c.c.) is added 10 c.c. sulphuric acid (1 : 1), 2 grams ferric sulphate, and 3 c.c. nitric acid, and the whole boiled till all iodine is expelled; 1 c.c. nitric acid is again added, and the solution again boiled. (ii.) The ferric sulphate and nitric acid of method (i.) are replaced by 2 grams of pure sodium nitrite (or, failing this, by passing into the solution the vapours generated from the slightly impure nitrite and dilute sulphuric acid).

Bromide and Iodide (*v. supra, Iodides*).

Bromide and Chloride. The solution is acidified so as to contain 25 c.c. of concentrated nitric acid in a total volume of 100 c.c., heated to boiling and boiled for one minute, the source of heat removed and air sucked through the solution until it is perfectly colourless (and for one minute longer). The bromine is then completely expelled; the residual *chloride* is titrated by Volhard's method. The *total halogens* are titrated in another portion of solution (J. Soc. Chem. Ind. 1909, 28, 505).

(For a very accurate but more elaborate method, *v.* J. Amer. Chem. Soc. 1907, 29, 275; also Zeitsch. anorg. Chem. 1895, 10, 387; Zeitsch. anal. Chem. 1900, 39, 81.)

Chloride, Bromide, and Iodide. (*a*) The *iodide* is decomposed with potassium iodate and acetic acid, the iodide extracted with chloroform and titrated. The *bromide* is destroyed by boiling with 5N-nitric acid, any iodate remaining is decomposed with a slight excess of potassium iodide, which excess is readily decomposed by boiling with nitric acid, and the residual *chloride*

titrated. The total *halogens* are titrated in another portion of solution (J. Amer. Chem. Soc. 1903, 25, 1138).

(*b*) The *iodide* is destroyed by boiling with ferric sulphate and sulphuric acid, and the amount of ferric salt reduced is determined with *N*/10-dichromate. The *total halogens* are determined by Volhard's method, and, in another portion of solution, the iodide is removed by adding hydrogen peroxide and acetic acid and distilling in steam, the bromine separated as described under *Bromide and Chloride* and the residual *chloride* titrated (J. Soc. Chem. Ind. 1909, 28, 505).

Iron. FERROUS SALTS. *By oxidation.* (*a*) The cold solution is strongly acidified with dilute sulphuric acid and titrated with *N*/10-permanganate. This simple and accurate method requires modification when hydrochloric acid is present, since it reacts with permanganate. This side-reaction can be practically prevented by adding a moderate quantity of manganese sulphate to the solution and titrating very slowly. A solution is prepared as follows: 67 grams of crystalline manganese sulphate are dissolved in water, 138 c.c. of phosphoric acid (sp.gr. 1·7), and 130 c.c. concentrated sulphuric acid (sp.gr. 1·82) are added, and the mixture diluted to 1 litre. Of this solution, 25 c.c. are added to the ferrous solution to be titrated. The phosphoric acid keeps the ferric solution colourless, and thus facilitates the observation of the end-point (Zeitsch. anal. Chem. 1863, 1, 329; Chem. Zeit. 1889, 13, 323; Amer. Chem. J. 1905, 34, 109; Analyst, 1908, 33, 43, and 1909, 34, 306).

(*b*) The acid solution is oxidised by *N*/10-dichromate as described under *Preparation of standard solutions.*

FERRIC SALTS. (*a*) *By reduction* to ferrous salt and titration with permanganate or dichromate. Reduction may be effected in any of the following ways: (i.) The sulphuric acid solution is heated to boiling and hydrogen sulphide passed through it until the solution is completely colourless; the excess of hydrogen sulphide is expelled from the boiling solution by a current of carbon dioxide. (ii.) The nearly neutral solution is boiled with sulphurous acid or ammonium sulphite, excess being removed by continued boiling, preferably in a current of carbon dioxide. (iii.) Eight or ten grams of granulated zinc are added to the warm sulphuric acid solution, and the action allowed to continue until a drop of the solution no longer gives a colouration with potassium thiocyanate. The solution is cooled, filtered through glass wool, and titrated. The use of the zinc-copper couple is preferable (Analyst, 1901, 26, 225; compare Chem. News, 1908, 97, 50). Reduction may be rapidly effected by pouring the liquid through a long column of zinc (The Jones' Reductor (Fig. 15); Chem. News, 1889, 60, 93; Blair's Chemical Analysis of Iron, 6th ed. 94). (iv.) The hydrochloric acid solution is heated nearly to boiling, and stannous chloride (25 p.c. solution) added drop by drop until the solution is colourless; 10 c.c. of saturated mercuric chloride are added to destroy excess of stannous chloride, the solution diluted, manganese sulphate added (*v. supra*), and the ferrous *salt titrated with N/10-permanganate* (Analyst, 1909, 34, 306). (v.) *Reduction by palladium-hydrogen* in boiling acid solution; this introduces no foreign substance into the

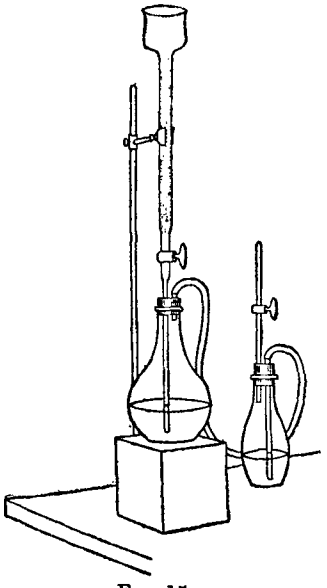


FIG. 15.

solution (Zeitsch. angew. Chem. 1902, 15, 398, 424; Analyst, 1904, 29, 346). (vi.) *Reduction with titanous sulphate* (Amer. J. Sci. 1908, 25, 343).

(*b*) *By direct titration with a reducing agent.* (i.) *Titanous chloride.* The sulphuric or hydrochloric acid solution of the ferric salt is titrated as described under *Preparation of standard solutions*, p. 205. (ii.) *Stannous chloride.* The nearly boiling hydrochloric acid solution is titrated as described under *Preparation of standard solutions*, p. 205, using either the mercuric chloride indicator (Amer. Chem. J. 1893, 15, 360) or titrating back with iodine.

FERROUS IRON IN MINERALS AND ROCKS. The only satisfactory method consists in decomposing the coarsely powdered substance with sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, and titrating the ferrous salt produced (*Cooke's Method*; Amer. J. Sci. 1867, 44, 347; *see* also Amer. J. Sci. 1894, 48, 149). The old method of heating with dilute sulphuric acid in a sealed tube (Mitscherlich) is worthless in the presence of sulphur or sulphides (J. Amer. Chem. Soc. 1900, 22, 625). (For an exhaustive discussion of this problem, *v.* Hillebrand's Analysis of Silicate and Carbonate Rocks.)

Iron and Aluminium. After weighing the ignited sesquioxides, they are brought into solution by fusion with potassium hydrogen sulphate or acid potassium fluoride (followed by evaporation with sulphuric acid), and the *iron* reduced and titrated (Zeitsch. angew. Chem. 1905, 18, 815).

Iron and Titanium. Ferric salts can be reduced with sulphurous acid or hydrogen sulphide without reducing *titanic* salts; or reduction of both may be effected with zinc and

sulphuric acid, the *titanous* salt oxidised with a slight excess of bismuth oxide, and the *ferrous* salt titrated in the filtered solution. To estimate both elements present, one of the preceding methods may be combined with the reduction process for titanium, described later, which would give the *total iron and titanium* (*v.* also J. Soc. Chem. Ind. 1909, 28, 189; Analyst, 1910, 35, 198).

Iron and Vanadium. Reduction with sulphur dioxide proceeds with the vanadium as far as to the oxide V_2O_4; reduction with zinc carries it as far as V_2O_2; hence two such reductions and titrations with permanganate furnish data for calculating both iron and vanadium (Amer. J. Sci. 1908, 26, 79).

Lead. *By precipitation* (i.) *As molybdate.* The boiling acetic acid solution is titrated with standard ammonium molybdate (4·75 grams per litre, titrated against pure lead) until a drop of solution gives a brown or yellow colour with a drop of dilute tannic acid solution. The indicator not being very sensitive, a 'blank' experiment should be made and the necessary correction allowed for both in an assay and in standardising the solution. (ii.) *As ferrocyanide.* The cold acetic acid solution is titrated with potassium ferrocyanide (10 grams per litre titrated against pure lead) until a drop of the solution produces a brown colouration with a drop of saturated uranium acetate solution; a 'blank' experiment should also be made (J. Amer. Chem. Soc. 15, 550; Chem. News, 1896, 73, 18). In determining lead in ores, &c., it is usually separated as sulphate and dissolved in ammonium acetate previous to titration. (For a comprehensive review of methods for lead, *v.* Chem. News, 1903, 87, 40; Gaz. chim. ital. 1896, 26, i. 327; *see* also *Methods of separation*; and J. Amer. Chem. Soc. 1903, 25, 632; 1904, 26, 1135.)

Magnesium. (*a*) *Acidimetrically.* The magnesium is precipitated as the double ammonium phosphate, the precipitate washed with dilute ammonia, and then with aqueous alcohol till free from extraneous ammonia, dissolved in a measured excess of $N/10$-hydrochloric acid, and the excess titrated with $N/10$-sodium hydroxide, using methyl orange for indicator:

$$Mg(NH_4)PO_4 + 2HCl = MgCl_2 + H_2(NH_4)PO_4$$

(Chem. Zentr. 1876, 727; for a method which obviates the use of alcohol, *v.* J. Amer. Chem. Soc. 1900, 22, 31; *see* also *Phosphorus*).

(*b*) *Iodimetrically.* The magnesium is precipitated as double ammonium arsenate, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated (J. Amer. Chem. Soc. 1899, 21, 746; Zeitsch. anal. Chem. 1907, 46, 714).

Manganese. (*a*) *By oxidation with permanganate.* (*Volhard's method, modified.*) The neutral chloride or sulphate solution containing 10 grams of zinc sulphate is heated to boiling, 1 gram of freshly ignited zinc oxide added, and the liquid titrated with $N/10$-permanganate, boiling and shaking frequently until the supernatant liquid is red; 1 c.c. pure glacial acetic acid is added, and the titration slowly finished with permanganate in the hot *but not boiling* liquid. The manganese can be accurately calculated from the equation:

$$3MnO + Mn_2O_7 = 5MnO_2$$

(Zeitsch. anal. Chem. 1909, 48, 751; Little and Cahen, Analyst, 1911, 36, 52).

(*b*) *By precipitation as dioxide* and estimation of the available oxygen. Precipitation may be effected in one of the following ways: (i.) By adding bleaching-powder solution and calcium carbonate to a hot neutral solution of the manganese salt containing ferric and zinc chlorides (Chem. Soc. Trans. 1879, 35, 365; J. Soc. Chem. Ind. 1891, 10, 333). (ii.) By boiling the solution in concentrated nitric acid (quite free from any hydrochloric acid) with potassium (or preferably sodium) chlorate. (iii.) By boiling the dilute sulphuric acid solution with ammonium persulphate (Zeitsch. angew. Chem. 1901, 14, 1149; 1903, 16, 905; Compt. rend. 1902, 135, 965; 1903, 136, 449). The washed precipitate in either case is dissolved in a sulphuric acid solution of standard ferrous sulphate or oxalic acid, and the excess of reagent titrated. The precipitate obtained by method (ii.) is deficient in available oxygen (Amer. J. Sci. 1898, *5*, 260), and the standard solution employed in the final titration must therefore be standardised on a known amount of manganese treated in a similar fashion.

(*c*) *By conversion into permanganic acid.* (i.) The cold solution free from hydrochloric acid, and containing one quarter its volume of nitric acid (specific gravity 1·42), is oxidised by shaking with 2–4 grams of sodium bismuthate for three minutes, diluted with half its volume of 3 p.c. nitric acid, the solid residue allowed to settle, and the permanganic acid solution filtered into a slight excess of ferrous sulphate; excess of the latter is then titrated with $N/10$-permanganate (Dingl. poly. J. 269, 224; Chem. Soc. Trans. 1895, 67, 268; Chem. News, 1901, 84, 209, 247; J. Amer. Chem. Soc. 1904, 26, 793). (ii.) The oxidation of small quantities of manganese may be effected by boiling the nitric acid solution with lead peroxide, or by heating with ammonium persulphate in the presence of a little silver nitrate (Chem. News, 1901, 84, 239).

Manganese in Ferromanganese and Steels. The foregoing methods *a*, *b*, and *c* (i.) have all been employed for this purpose; method *c* (i.) is the simplest and probably the most accurate. In method *a* it is necessary to remove iron from the solution; this is conveniently performed by adding a slight excess of zinc oxide to the solution (*v.* references given above; also J. Amer. Chem. Soc. 1902, 24, 243; Ann. Chim. anal. 1906, 11, 124).

Manganese and Chromium occurring together in steels may be estimated by oxidising with ammonium persulphate in sulphuric acid solution in the presence of silver nitrate; one portion of solution is titrated for total permanganate and chromate with ferrous sulphate, and another for permanganate alone by means of arsenious oxide (J. Amer. Chem. Soc. 1905, 27, 1550; *v.* also Chem. News, 1901, 83, 25; 1905, 91, 3; Chem. Zeit. 1905, 29, 987; Chem. Zeit. Rep. 1905, 29, 380).

The foregoing bismuthate method *c* (i.) may be applied in the presence of *molybdenum*, *tungsten*, *titanium*, and *vanadium*; also, with certain precautions, in the presence of *chromium* (Chem. News, 1901, 84, 247). (For estimating *manganese*

in *tungsten steels*, *v.* also J. Soc. Chem. Ind. 1907, 26, 345.)

Mercury. (*a*) *By precipitation.* Mercuric nitrate is readily titrated with *N*/10-thiocyanate, using ferric nitrate as indicator, provided that nitric acid is present in fairly high concentration (Ber. 1901, 34, 3502; 1902, 35, 2015). Chloride must be absent; if necessary, the mercury is precipitated as oxide with sodium hydroxide, and the washed precipitate dissolved in nitric acid.

(*b*) *Iodimetrically.* The mercuric solution (25–50 c.c.) containing 1 gram of potassium iodide is made alkaline with sodium hydroxide, 2–3 c.c. of 40 p.c. formaldehyde added, and the whole shaken vigorously for two minutes. The solution is acidified with acetic acid, and the reduced mercury is dissolved by adding an excess of *N*/10-iodine. After shaking, the excess of iodine above that required to form mercuric iodide is titrated with *N*/10-thiosulphate (Ber. 1906, 39, 3702; 1907, 40, 3276; *Bull.* Soc. chim. 1907, [iv.] 1, 1169). *Mercurous salts* require a preliminary oxidation.

(For other methods, *v.* Compt. rend. 1863, 56, 63; Chem. Soc. Trans. 1892, 61, 364; Arch. Pharm. 241, 444.)

Molybdenum. (*a*) *By reduction and subsequent oxidation.* The sulphuric acid solution is reduced by passing it through a long column of amalgamated zinc to a condition represented by the formula Mo_2O_3; the liquid is caught directly in ferric sulphate solution, which reoxidises the molybdenum salt, and the ferrous sulphate produced is titrated with *N*/10-permanganate (Amer. J. Sci. 1907, 24, 313; compare Ber. 1905, 38, 604; Analyst, 1907, 32, 250).

(*b*) *Iodimetrically.* The solution in concentrated hydrochloric acid is boiled with a slight excess of potassium iodide till the volume is reduced to 25 c.c., when complete reduction to the condition Mo_2O_5 is effected. The solution is cooled, diluted to 125 c.c., 0·5 gram of manganese sulphate added, and then a slight excess of *N*/10-permanganate; *N*/10-arsenious acid is next added, and after the addition of tartaric acid and sodium bicarbonate, the excess is titrated with *N*/10-iodine. The permanganate *plus* iodine and *minus* the arsenious acid measure the Mo_2O_5 present (Amer. J. Sci. 1901, 12, 449; compare *ibid.* 1896, 2, 156; 1898, 6, 168).

Molybdenum in Steels and Alloys (*v.* J. Amer. Chem. Soc. 1904, 26, 675).

Nickel. (*a*) *By double cyanide formation.* A few drops of 10 p.c. potassium iodide are added to the cold, slightly ammoniacal nickel solution, and then a small measured volume of silver nitrate (3 grams of silver per litre). Standard potassium cyanide (25 grams per litre) is then run in with stirring till the precipitate of silver iodide just disappears; more silver nitrate is added till a very faint turbidity is produced, which is then dissolved by the least possible excess of cyanide. The relative values of the silver nitrate and cyanide solutions are determined by a preliminary experiment, and the cyanide standardised against a known amount of pure nickel (or pure silver, and calculated to nickel). The method is rapid and accurate (Chem. News, 1895, 72, 92).

(*b*) *By precipitation.* The hot nickel solution containing ferric chloride and citric acid is made feebly ammoniacal and titrated slowly, stirring constantly, with standard potassium ferrocyanide (20 grams per litre, titrated against pure nickel), until a drop of the solution when acidified with dilute acetic acid develops a green colour in five minutes (J. Amer. Chem. Soc. 1910, 32, 757; Bull. Soc. chim. 1907, 4, 1163).

Nickel in Steel. Method (*b*) can be directly applied; method (*a*) can also be employed without removing iron, molybdenum, or chromium, if a sufficient excess of ammonium citrate or sodium pyrophosphate is added to the solution; or a moderate amount (2–3 grams) of each of these reagents may be added (J. Amer. Chem. Soc. 1907, 29, 1201; 1908, 30, 1116; 1899, 21, 854; Chem. Zeit. 1908, 32, 1223). (For modifications in presence of other metals, *v.* Chem. News, 1898, 78, 177, 190.)

Nitrogen. AMMONIA (*v.* ACIDIMETRY AND ALKALIMETRY).

HYDRAZINE. *Iodimetrically.* A moderate excess of sodium bicarbonate or sodium acetate is added to the solution of a hydrazine salt, which is then titrated with *N*/10-iodine. $N_2H_4=21$ (J. pr. Chem. 1902, 66, 332; 1903, 67, 140; *v.* also Gazz. chim. ital. 1899, 29, 265).

HYDROXYLAMINE. (*a*) *By oxidation.* The solution of a hydroxylamine salt is slowly added to excess of boiling and well stirred Fehling's solution, the precipitated cuprous oxide washed, dissolved in acid ferric alum, and the ferrous salt titrated with permanganate. $NH_2OH=Cu_2$ (Chem. Soc. Trans. 1903, 83, 1394; compare Ber. 1877, 10, 1940).

(*b*) *By reduction.* An excess of titanium sesquisulphate is added to the acid solution, and the ammonium salt produced is estimated by distillation with sodium hydroxide (Ber. 1909, 42, 2695).

NITRATES. (*a*) *By reduction.* The solution is made strongly alkaline with sodium hydroxide, 5 c.c. of alcohol and 2·5–3 grams of powdered Devarda's alloy added, and the flask connected with a distilling apparatus, the receiver of which contains excess of *N*/2-hydrochloric acid. After standing for half an hour, the liquid is steam-distilled for an equal length of time, when all the nitrate has been converted into ammonia and driven over into the acid; the excess of the latter is then titrated (Zeitsch. anal. Chem. 1894, 33, 113; Analyst, 1910, 35, 307; *v.* also the *Gravimetric section*).

(*b*) *Iodimetrically* (*v.* Zeitsch. angew. Chem. 1890, 3, 477; Chem. Soc. Trans. 1891, 59, 530; Amer. J. Sci. 1892, 44, 117).

NITRITES. (*a*) *By oxidation.* The nitrite solution is slowly added to a measured quantity of *N*/10-permanganate, which is acidified with sulphuric acid, diluted to 400 c.c., and warmed to 40°, until the colour is just discharged. $2HNO_2 = O_2$. Otherwise, the cold dilute nitrite solution is slowly titrated with *N*/10-permanganate to a red colouration; a few drops of sulphuric acid are then added, followed by an excess of permanganate. The liquid is then strongly acidified with sulphuric acid, heated nearly to boiling, and the excess of permanganate titrated with *N*/10-oxalic acid (Amer. Chem. J. 1883, 5, 388).

(*b*) *Iodimetrically.* Several methods have been based on the reaction.

$$2HI+2HNO_2 = I_2+2NO+2H_2O.$$

It is necessary to perform the experiment in an atmosphere free from oxygen; the iodine may be determined by thiosulphate or arsenite. (For details, *v.* Pharm. J. 19, 741; Chem. News, 1904, 90, 114; cf. *Organic analysis*, Aromatic amines.)

Osmium. *Iodimetrically* (*v.* Chem. Zentr. 1898, ii. 65).

Oxygen. PEROXIDES. (*a*) *Iodimetrically.* Such peroxides as those of manganese and lead may be estimated by distillation with concentrated hydrochloric acid, and collecting the chlorine evolved in potassium iodide (*Bunsen's method*). Finely divided peroxides of manganese react quantitatively with cold dilute hydrochloric acid and potassium iodide (Chem. Soc. Trans. 1880, 37, 128), a method of estimation that is available with the peroxides of the alkali and alkali earth metals, which do not give satisfactory results by the distillation method (Arch. Pharm. 1902, 240, 437). Hydrogen peroxide may be determined in this manner (Analyst, 1888, 13, 62).

(*b*) *By reduction.* Hydrogen peroxide, or peroxides of the alkal and alkaline-earth metals, may be dissolved in cold dilute acid and titrated with *N*/10-permanganate, which loses as much oxygen as is lost by the peroxide (*v.* also *Gas-Volumetric methods*).

(For critical reviews of methods, &c., *v.* Arch. Pharm. 228, 432; Amer. Chem. J. 1906, 36, 117; Zeitsch. angew. Chem. 1901, 14, 828; 1908, 21, 589; Chem. Zeit. 1906, 30, 1275; 1907, 31, 1257; Zeitsch. anal. Chem. 1908, 47, 465.)

Phosphorus. PHOSPHORIC ACID (ORTHO-). (*a*) (*v.* ACIDIMETRY AND ALKALIMETRY).

(*b*) *Acidimetrically, with previous precipitation.* (i.) The precipitated magnesium ammonium phosphate (*v. Gravimetric section*) is washed and titrated as described under *Magnesium*, p. 212 (Zeitsch. anal. Chem. 1898, 37, 217; Zeitsch. angew. Chem. 1905, 18, 655; compare Zeitsch. anal. Chem. 34, 33). (ii.) The precipitate of ammonium phosphomolybdate (*v. Gravimetric section*) after washing is dissolved in a slight excess of standard potassium hydroxide free from carbonate, and the excess titrated with standard nitric acid using phenolphthaleïn as indicator. One molecular proportion of P_2O_5 present as $(NH_4)_3PO_4,12MoO_3$, requires 23 molecules of K_2O in pure aqueous caustic potash. $P_2O_5=23K_2O$ (J. Amer. Chem. Soc. 1895, 17, 950; 1897, 19, 703; J. Soc. Chem. Ind. 1904, 23, 1186).

(*c*) *By precipitation.* To the solution, feebly acid with acetic acid, 10 c.c. of 10 p.c. ammonium acetate are added and standard uranium acetate solution (35 grams per litre) run in from a burette until a drop of the solution gives a brown colouration with potassium ferrocyanide upon a white tile. The solution is heated to boiling, when the latter reaction will no longer take place, and more uranium acetate added until the brown colouration is obtained once more, *e.g.*:

$$KH_2PO_4+UO_2(C_2H_3O_2)_2+NH_4{\cdot}C_2H_3O_2 = KC_2H_3O_2+2HC_2H_3O_2+UO_2NH_4PO_4$$

In analysing alkali phosphates, the uranium solution is standardised against pure potassium dihydrogen phosphate, while a solution of calcium phosphate in acetic acid, standardised gravimetrically by the method of Woy (Chem. Zeit. 1897, 21, 442), must be used if the uranium acetate is to be used for estimating phosphates of the alkaline earths (J. Soc. Chem. Ind. 1892, 11, 328). It is essential that titrations should be made under conditions closely approximating those which obtained when the uranium solution was standardised.

PHOSPHORUS IN IRON AND STEEL. This is usually separated as ammonium phosphomolybdate; it may then be titrated according to *b* (ii.) above, or the precipitate is washed with dilute ammonium sulphate, dissolved in ammonia, the solution strongly acidified with sulphuric acid, reduced with zinc, and the Mo_2O_3 solution collected directly in ferric alum, the ferrous salt being then titrated as described under *Molybdenum* (Amer. J. Sci. 1907, 24, 313; compare Blair's Analysis of Iron).

Potassium. *By oxidation.* The acetic acid solution, free from ammonium salts, is evaporated on the water-bath till pasty with sodium cobaltinitrite solution in rather large excess, cooled and stirred with 50–100 c.c. of cold water. The dipotassium sodium cobaltinitrite is collected, on asbestos, washed with cold water, and then immersed in an excess of nearly boiling permanganate solution. After 5 minutes the solution is acidified with sulphuric acid, excess of *N*/10-oxalic acid added, and the clear solution titrated with permanganate. The permanganate is best standardised against a pure potassium salt. The oxidation of 2 molecular porportions of $K_2NaCo(NO_2)_6$ by permanganate requires 11 atomic proportions of oxygen or 4K = 22H (Amer. J. Sci. 1907, 24, 433; compare Chem. Soc. Trans. 1900, 77, 1076). (For another method, *v.* Chem. Zeit. 1895, 19, 301.)

Selenium. SELENIOUS ACID. *By oxidation.* To the cold solution containing 5 p.c. by volume of concentrated sulphuric acid is added an excess of *N*/10-permanganate; a moderate excess of *N*/10-oxalic acid is then added, and the titration finished at 50°–60° with permanganate. $2SeO_2 = O_2$ (Amer. J. Sci. 1895, 50, 51).

(For an entirely different method, *v.* Amer. Chem. J. 1896, 18, 703; Amer. J. Sci. 1899, 7, 287.)

SELENIC ACID. *Iodimetrically.* (i.) The acid is boiled with hydrochloric acid (25 c.c. concentrated acid in a total volume of 75 c.c.) for 10 minutes in a Bunsen distilling apparatus or one of its various modifications, and the chlorine evolved is collected in potassium iodide (*v. supra, Volumetric estimation of halogens*, p. 209) $SeO_3 = Cl_2$ (Amer. J. Sci. 1895, 50, 400). (ii.) The solution (60 c.c.) containing 20 c.c. of sulphuric acid (1 : 1) and 1 gram of potassium bromide is distilled and the liberated bromine collected in potassium iodide. $SeO_3 = Br_2$ (Amer. J. Sci. 1895, 50, 402).

SELENIUM IN EITHER STATE OF OXIDATION. *Iodimetrically.* This is effected by a Bunsen distillation, the solution (60 c.c.) containing 5 c.c. of concentrated hydrochloric acid and 1–3 grams of potassium iodide. The selenium compound is reduced to the element itself, and an equivalent of iodine is distilled into potassium iodide and titrated. $SeO_2 = 2I_2$ and $SeO_3=3I_2$ (Amer. J. Sci. 1895, 50, 249; for a simpler method *v.* Amer. J. Sci. 1896, 1, 31).

Silver. *By precipitation.* (i.) The nitric acid solution is titrated with standard sodium chloride until no further precipitation is observed. (For details of this very exact method, *v.* the article on ASSAYING.) A number of devices have been described for rapidly filtering a portion of the liquid in order to test it for further precipitation (Chem. Soc. Trans. 1908, 93, 1037; Gazz. chim. ital. 1909, 39, ii. 240). A modified method consists in adding a slight deficit of sodium chloride, filtering and titrating the remaining silver with dilute ammonium thiocyanate (J. Amer. Chem. Soc. 1897, 19, 814; *v.* also Chem. Soc. Trans. 1900, 77, 232; Zeitsch. angew. Chem. 1904, 17, 647). (ii.) Titration may be effected with *N*/10-thiocyanate as described under *Preparation of standard solutions.*

Sodium (*v.* Chem. Soc. Trans. 1898, 73, 167).

Sulphur, Acids of. HYDROGEN SULPHIDE. *Iodimetrically.* The gas or a measured volume of solution is absorbed in an excess of *N*/10-iodine, the excess being afterwards titrated with *N*/10-thiosulphate. $H_2S = I_2$. Direct titration with iodine leads to low results (Zeitsch. anal. Chem. 1906, 45, 541).

HYDROSULPHUROUS ACID. *By oxidation.* The sodium salt, used in indigo-dyeing, can be estimated by dissolving it in air-free water in an atmosphere of carbon dioxide, adding a drop of ferrous sulphate, and running in standard potassium ferricyanide solution until a blue colour appears, air being rigidly excluded (Zeitsch. angew. Chem. 1905, 18, 168):

$$Na_2S_2O_4+2K_3Fe(CN)_6=2SO_2+2K_3NaFe(CN)_6.$$

If necessary, a little acetic acid is added to ensure that the liquid shall be acid.

SULPHUROUS ACID. *Iodimetrically.* An aqueous solution of sulphur dioxide is estimated by running it into an excess of standard iodine solution with constant stirring, and not *vice versâ*, since that method causes a separation of sulphur due to the side-reaction:

$$SO_2+4HI=S+2H_2O+2I_2$$

(Annalen, 1887, 242, 94). Sulphites may be accurately determined by adding the powdered salt to excess of *N*/10-iodine, and after the decomposition is complete, titrating back with *N*/10-thiosulphate (J. Soc. Chem. Ind. 1884, 3, 197; 1885, 4, 303)

$$SO_2+I_2+2H_2O = H_2SO_4+2HI.$$

SULPHURIC ACID. (*a*) *Iodimetrically.* The feebly acid boiling dilute sulphate solution is precipitated with an excess of a solution of barium chromate in hydrochloric acid (3–4 grams $BaCrO_4$, 30 c.c. conc. HCl, diluted to 1 litre). Barium sulphate is thus precipitated, and an equivalent of chromic acid liberated. The boiling solution is neutralised with powdered chalk to remove excess of barium chromate, and the chromic acid in the cold filtrate titrated iodimetrically. $CrO_3=SO_3$ (Amer. Chem. J. 1889, 11, 567; Chem. Zeit. 1898, 22, 357).

(*b*) *By precipitation.* (i.) The boiling sulphate solution, slightly acid with hydrochloric acid, is titrated with standard barium chloride until no more precipitate is produced. $Ba=SO_4$ (Chem. News, 1889, 59, 41). A device for readily observing the end-point is described in Chem. Soc. Trans. 1907, 91, 1370. (ii.) Method (i.) may be modified by adding an excess of barium chloride, and determining the excess by adding sodium acetate, acetic acid, and ammonium dichromate, and titrating an aliquot part of the filtrate with *N*/20-ferrous sulphate (Chem. Soc. Trans. 1909, 95, 2198). (iii.) The sulphate is precipitated from dilute solution with excess of benzidine hydrochloride solution as benzidine sulphate, and the precipitate titrated with *N*/10-sodium hydroxide, using methyl orange as indicator (*v.* Zeitsch. angew. Chem. 1907, 20, 9, for details, corrections, &c.).

THIOSULPHURIC ACID. *Iodimetrically.* Thiosulphates are titrated with iodine as in standardising thiosulphate solution (*v. supra*, p. 205); sparingly soluble salts are suspended in water and titrated, shaking vigorously in a stoppered bottle all the time.

PERSULPHURIC ACID. (*a*) *By oxidation.* The solution is acidified with sulphuric acid, a considerable excess of standard ferrous sulphate is added, and then 100 c.c. of hot distilled water (70°–80°). Excess of ferrous salt is then quickly titrated with *N*/10-permanganate. $H_2S_2O_8=2FeO$ (Chem. Soc. Abst. 1900, ii. 45).

(For other methods, *v.* Chem. Zentr. 1900, 435; Amer. J. Sci. 1901, 12, 367; Gazz. chim. ital. 1902, 32, ii. 383; Bull. Soc. chim. 1903, 30, 930.)

Tellurium. TELLUROUS COMPOUNDS. (*a*) *By oxidation.* The solution is rendered alkaline with sodium hydroxide, an excess of *N*/10-permanganate is added, and the excess estimated by acidifying with sulphuric acid, adding *N*/10-oxalic acid in excess, and finishing the titration with permanganate. $2TeO_2=O_2$ (Chem. Soc. Trans. 1891, 59, 238; Amer. J. Sci. 1899, 8, 122).

(*b*) *By precipitation* as tetraiodide in moderately concentrated sulphuric acid solution (Amer. J. Sci. 1896, 2, 271).

(*c*) *Iodimetrically* (*v.* Amer. Chem. J. 1898, 20, 278).

TELLURIC COMPOUNDS. *Iodimetrically.* The tellurate is distilled with concentrated hydrochloric acid in Bunsen's apparatus, the chlorine absorbed in potassium iodide and the iodine set free is titrated with *N*/10-thiosulphate. Telluric anhydride must be previously dissolved in concentrated potassium (not sodium) hydroxide, since it is scarcely attacked by hydrochloric acid. The reduction, which proceeds to tellurous acid, may be also effected by distilling with potassium bromide and dilute sulphuric acid (Zeitsch. anorg. Chem. 1894, 7, 132).

Thallium. *Iodimetrically.* The dilute solution of thallic salt is mixed with excess of potassium iodide, and the iodine liberated is titrated with *N*/10-thiosulphate. $Tl = I_2$ (Compt. rend. 1902, 134, 655).

Tin. STANNOUS SALTS. *Iodimetrically.* The cold hydrochloric acid solution of the stannous salt is titrated with *N*/10-iodine. $Sn = I_2$ (J. Amer. Chem. Soc. 1897, 19, 809). Free exposure of the solution to air must be avoided, since stannous salts readily undergo oxidation; it is preferable to work in an atmosphere of carbon dioxide.

STANNIC SALTS must be reduced before titration with iodine; this may be accomplished by heating the hydrochloric acid solution with iron, or sheet nickel, or with finely powdered antimony (Chem. News, 1901, 84, 167).

Titanium. *By reduction and subsequent oxidation.* It is difficult to obtain accurate results with quantities of titanium dioxide exceeding 0·15 gram. The warm, dilute sulphuric acid solution of titanic salt is reduced to the tervalent condition by means of zinc, aluminium-magnesium alloy, or zinc-aluminium alloy (Zn, 90 p.c. Al 10 p.c., cast in sticks), cooled and rapidly filtered into ferric sulphate solution; the equivalent quantity of ferrous sulphate produced is titrated with N/10-permanganate. Ti = Fe (Chem. Zeit. 1907, 31, 399; Amer. J. Sci. 1908, 25, 130; Analyst, 1910, 35, 198; compare J. Amer. Chem. Soc. 1895, 17, 878).

Titanium and Iron (*v. Iron*).

Tungsten. *By reduction and subsequent oxidation.* The solution is reduced by zinc and hydrochloric acid to a condition corresponding to the oxide WO_2, filtered and titrated with a standard ferric solution. The end-point is perceived by the disappearance of the intense blue colour of the intermediate compound corresponding to W_2O_5, the reaction

$$Fe_2O_3+WO_2 = WO_3+2FeO$$

being quantitative (Chem. Soc. Proc. 1909, 25, 227).

Uranium. (*a*) *By reduction and subsequent oxidation.* The solution, containing 20 c.c. of concentrated sulphuric acid in a volume of 125 c.c., is poured upon 100 grams of pure zinc (in sticks 2 cm. long), heated nearly to boiling for 15 minutes, filtered into a large porcelain dish, and the zinc washed with cold dilute sulphuric acid (1 : 10 by volume) till the total volume of solution is 300 c.c. The solution of uranous sulphate, which should be sea-green in colour, is then titrated with N/10-permanganate. The solution can also be reduced by passage through a long column of amalgamated zinc; in either case the reduction proceeds a little too far, but oxidation to the uranous state is accomplished during the filtration and washing. High results are obtained by carrying out the experiment in an atmosphere of carbon dioxide.

$5U(SO_4)_2 = 2KMnO_4 = 10FeSO_4$, or $U = 2Fe$

(J. Amer. Chem. Soc., 1909, 31, 367; compare *ibid.* 1901, 23, 685; 1906, 28, 1541; Amer. J. Sci. 1903, 16, 229).

(*b*) *Iodimetrically* (*v.* Ber. 1904, 37, 189).

Uranium and Vanadium (*v.* J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium. (*a*) *By reduction and subsequent oxidation.* (i.) The vanadic solution containing sulphuric acid is boiled with sulphur dioxide until the colour is a pure blue, and the excess of sulphur dioxide then expelled with carbon dioxide; the solution, containing vanadium salt corresponding to the oxide V_2O_4, is then titrated hot with N/10-permanganate. (ii.) The sulphuric acid solution is passed through a long column of amalgamated zinc, and the reduced solution collected and titrated as described under *Molybdenum* (*v. supra*, p. 213). In this case reduction proceeds as far as the oxide V_2O_2 (Amer. J. Sci. 1908, 25, 332; compare *ibid.* 1903, 15, 389). (iii.) The solution is evaporated nearly to dryness three times with concentrated hydrochloric acid, when vanadyl chloride $VOCl_2$ is formed; hydrochloric acid is removed by evaporation with sulphuric acid, the solution diluted and titrated with N/10-permanganate (Ber. 1903, 36, 3164).

(*b*) *By reduction.* The vanadate solution, hot or cold, and containing hydrochloric or sulphuric acid, is titrated with standard (2 p.c.) stannous chloride (titrated against iodine) until a drop of the solution gives a blue colouration with ammonium molybdate. Reduction proceeds as far as the tetroxide V_2O_4 (Bull. Soc. chim. 1908, 3, 626).

(*c*) *Iodimetrically.* (i.) About 0·3–0·5 gram of vanadate is distilled with 1·5–2·0 grams of potassium bromide and 30 c.c. of concentrated hydrochloric acid, the liberated bromine absorbed in potassium iodide, and the iodine titrated with N/10-thiosulphate; $V_2O_5 = Br_2$, the reduction proceeding to the tetroxide (Chem. Zentr. 1890, i. 977; for other iodimetric methods, *v.* Amer. J. Sci. 1896, 2, 185, 355; 1902, 14, 369).

Vanadium and Chromium (*v.* Bull. Soc. chim. 1904, 31, 962).

Vanadium and Uranium (*v.* J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium and Iron (*v. Iron*; and J. Amer. Chem. Soc. 1908, 30, 1229, 1233).

Zinc. (*a*) *By precipitation.* The chloride solution, containing 3 c.c. of concentrated hydrochloric acid in a volume of 250 c.c., is heated nearly to boiling, and titrated with standard potassium ferrocyanide solution (21·5 grams per litre, titrated against pure zinc) until one or two drops of the solution produce a brown colouration with uranium nitrate (J. Amer. Chem. Soc. 1900, 22, 198; 1904, 26, 4; 1908, 30, 225; Zeitsch. anal. Chem. 1906, 44, 174). The uranium nitrate indicator may be replaced by ammonium molybdate (Chem. Zeit. 1905, 29, 951). It has been recommended to add excess of ferrocyanide, and titrate back with standard zinc chloride (Zeitsch. anal. Chem. 1896, 35, 469).

(For the application of this method to ores and alloys, *v.* J. Amer. Chem. Soc. 1907, 29, 265; Chem. Zeit. 1905, 29, 951; J. Soc. Chem. Ind. 1905, 24, 228, 1278.)

(*b*) *Acidimetrically.* As for *Magnesium*, *v. supra*, p. 212; and J. Amer. Chem. Soc. 1901, 23, 468.

(*c*) *Iodimetrically.* As for *Magnesium*, *v. supra*, p. 212; and J. Amer. Chem. Soc. 1900, 22, 353.

Colorimetric Methods.

These methods are especially valuable for the estimation of very small quantities of substances, and are capable of giving very accurate results. The depth of tint produced by some characteristic colour reagent in a given volume of the solution is compared with the tint produced by the same reagent in an equal volume of a solution containing a known quantity of the substance to be determined. The tint in the comparison tube can be varied by varying the proportion of the substance which it contains, and when the tints are equal the quantities of the substance in each tube are also equal. The quantity in one tube is known, and hence that in the other is determined. It is important that the comparison be made under comparable conditions with respect to degree of acidity or alkalinity, proportion of the reagent, and the

like. It is also important that the depth of tint should not be materially affected by the presence of other saline substances in the solution under examination.

The following substances may be determined by these methods :—

Lead, with hydrogen sulphide.

Copper, with hydrogen sulphide or potassium ferrocyanide (Carnelley, Chem. News, 32, 308).

Iron, with potassium ferrocyanide (Carnelley, Chem. News, 30, 257).

Iron, with potassium thiocyanate (Thomson, Chem. Soc. Trans. 1885, 493).

Vanadium, with hydrogen peroxide.

Titanium, with hydrogen peroxide (Weller, Ber. 1882, 15, 2593).

Ammonia, by Nessler's solution (*v.* WATER).

Iodine, in solution in carbon disulphide, or with starch.

Nitrates, by phenolsulphonic acid test (*v.* WATER).

Nitrites, by (i.) *m*-phenylenediamine; (ii.) sulphanilic acid and α-naphthylamine (*v.* WATER).

The principle may likewise be applied to the comparison of colouring matters, provided that the solutions are sufficiently diluted (*v.* COLORIMETER).

ULTIMATE ANALYSIS OF CARBON COMPOUNDS.

The majority of carbon compounds contain carbon, hydrogen, and oxygen, or carbon, hydrogen, oxygen, and nitrogen; a smaller number contain one or more of the halogens, or sulphur. There are a still smaller number of organic derivatives of phosphorus, arsenic, antimony, silicon, and other metalloidal and metallic elements, and the metals also occur in the salts of organic acids.

Qualitative Examination.

Carbon is converted into carbon dioxide when the substance is heated with cupric oxide.

Hydrogen. The substance is heated to a temperature below that at which decomposition begins, until all water existing as such is expelled, and is then heated with finely divided and recently ignited cupric oxide; the hydrogen is evolved as water.

Nitrogen. Many carbon compounds containing nitrogen evolve this element in the form of ammonia when heated with caustic soda or soda-lime, but this test is not applicable to nitro-, nitroso-, azo-, and diazo- derivatives.

Many nitro-, nitroso-, and diazo- derivatives evolve oxides of nitrogen, with or without explosion, when heated.

Nitrogen in all classes of carbon compounds, with the exception of the diazo- compounds, may be detected by heating the substance with metallic sodium or potassium, together with some sodium carbonate if the substance is explosive. The nitrogen is converted into alkali cyanide, and the cooled mass is extracted with water and the cyanogen detected by the Prussian-blue test, which consists in adding ferrous sulphate to the alkaline solution after filtration, warming gently and then acidifying. Nitrogenous carbon compounds containing sulphur yield, when heated with sodium, a thiocyanate, and the Prussian-blue test cannot be used. A large excess of potassium is recommended in this case, when it is stated that sulphur does not interfere (Täuber, Ber. 1899, 32, 3150). A mixture of potassium carbonate (138 parts) and magnesium powder (72 parts) has been recommended for general use in detecting nitrogen even in the case of diazo- derivatives and stable pyrrole compounds (*v.* Ber. 1902, 35, 2523; Gazz. chim. ital. 1904, 34, [2] 359). This mixture is, however, found to take up nitrogen from the atmosphere (Ellis, Chem. News, 1910, 102, 187).

Halogens are detected by heating the substance with pure lime or pure soda-lime, extracting with water, slightly acidifying with nitric acid, and testing with silver nitrate. Highly nitrogenous compounds, when heated with lime, are apt to yield calcium cyanide; hence the supposed precipitate of silver halide should always be tested for cyanide (*v. Separation of cyanide and chloride*), unless nitrogen is known to be absent. With soda-lime no cyanide is formed. The substance may also be heated with sodium or potassium as in testing for nitrogen; iodine and bromine are detected by acidifying, adding chlorine water, and shaking up with chloroform, which becomes purple or brown. The supposed silver chloride should, however, always be tested for cyanide.

Sulphur and phosphorus in non-volatile substances are detected by fusing with caustic soda or potash mixed with about one-fifth its weight of potassium nitrate, or by heating with sodium peroxide diluted with sodium carbonate; in either case the product is tested for sulphuric or phosphoric acid. Volatile or non-volatile substances may be oxidised by heating in a sealed tube at 150°–300°, according to circumstances, with fuming nitric acid of sp.gr. 1·5. Sulphur and phosphorus are oxidised to sulphuric and phosphoric acid respectively.

Sulphur is also detected by heating the substance with sodium, extracting with water, and adding sodium nitroprusside, when a brilliant violet colouration indicates the presence of alkaline sulphide.

Arsenic and antimony are detected by fusing the substance with equal weights of sodium carbonate and sodium peroxide, extracting with water, acidifying, and passing in hydrogen sulphide. Other appropriate tests for these two elements may be applied.

Quantitative Determinations.

Carbon and hydrogen in absence of nitrogen, halogens, &c.

The simplest and most convenient method for general purposes is to burn the compound in a glass tube in a current of oxygen, assisted by cupric oxide; the carbon is converted into carbon dioxide, which is absorbed by caustic potash; the hydrogen is converted into water, which is absorbed by calcium chloride or concentrated sulphuric acid.

Erlenmeyer's modification of Von Babo's furnace is frequently employed. The heat is supplied by a row of 20–25 Bunsen burners, each of which is provided with a tap and a perforated collar for regulating the supply of air. The flames strike the under side of a semicircular fireclay or sheet-iron trough or gutter in which the combustion tube rests on a layer of magnesia or asbestos. Inclined at an angle over this gutter on either side is a row of fireclay tiles

by which the flame is reverberated upon the upper part of the glass tube, which is thus heated all round. Each tile can be pulled back and rested against an iron rail which runs down each side of the furnace, and thus any part of the tube can be readily examined, and moreover the tiles can be made to assist in regulating the temperature.

In Hofmann's furnace the tube is heated by two double rows of perforated cylindrical fireclay burners placed over ordinary fish-tail burners. The tube rests upon the top of a central row of much shorter burners. The burners are inclosed by flat vertical tiles, and flat tiles are laid horizontally on the top.

In the Glaser furnace the heat is provided by a row of Bunsen burners. The tube is supported by a series of semicircular perforated iron plates, placed close together. The flames strike the bottom of these plates, and then pass through the perforations and strike against the fireclay covers, by which they are reverberated on the tube, so that the latter is heated from the top and sides as well as from the bottom. The tube is usually wrapped round with wire gauze. This furnace will give higher temperatures than the Erlenmeyer furnace, but consumes more gas.

A more modern type of combustion furnace which gives very high temperatures with a small consumption of gas has been introduced by Fletcher. The furnace itself consists of six separate hollow fireclay blocks 6 inches in length and of the same height, which are placed end to end, so as to give a total length of 3 feet. The combustion tube is supported on a fireclay trough placed along the top of the row of furnace blocks which are each pierced along one side with five holes leading to a hollow space immediately below the trough. The main gas-supply pipe is a brass tube of square section which is raised about 1½ inch above the stone

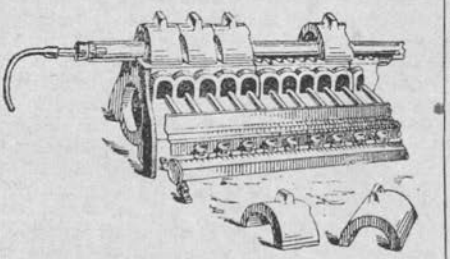


FIG. 16.

bench by terminal brass supports; it carries thirty burners projecting at right angles from it in a slanting direction, so that their nozzles reach upwards to the perforations in the furnace blocks, the centres of these holes being about 3½ inches above the bench. Each furnace block is therefore heated by five burners, and reverberation is ensured by small semicircular fireclay arches, three of which fit loosely on each of the furnace blocks. Owing to their oblique position, the burners are readily kept clean, the brass heating arrangement is quite separate from the earthenware furnace, and the taps and lower parts of the burners are protected from the heat of the furnace by a brass shield running along the whole length of the main gas pipe. The furnace can be built up in shorter lengths by using fewer of the furnace blocks, of which two are represented in Fig. 16.

To avoid the necessity for using an india-rubber stopper between the combustion tube and the water-absorption apparatus, Marek suggests a mercury joint made by drawing out the combustion tube to a conical end, and fixing round this a knee tube by means of asbestos and fused silver chloride. The knee joint, which is loosely filled with silver ribbon, fits into a bell-shaped tube dipping under mercury (J. pr. Chem. 1907, [2] 76, 180).

The combustion tube should consist of infusible potash or Bohemian glass 1·5–2 mm. thick, with an internal diameter of 12–15 mm. It should be of such a length that it projects about 2 cm. from each end of the gutter or trough. Pieces of copper wire gauze about 2 cm. broad, heated in a flame to remove grease, are rolled up into plugs which fit moderately tightly in the tube, and one of these plugs is pushed into the tube to a distance of about 25 cm. from one end. The tube is then filled with freshly ignited granular cupric oxide to within 5 or 6 cm. of the other end, and a second plug is inserted. The granules of cupric oxide should be fairly regular in size, and 1·5–2 mm. cube. Another plug about 10 cm. long is made by rolling a piece of copper gauze round a stout copper wire 12 cm. long, and bending the projecting end of the latter into a loop by means of which it can be withdrawn from the tube. This plug is placed in the other end of the tube behind the boat. The end of the tube nearest to the copper oxide is fitted with a dry caoutchouc stopper perforated to receive the tube of the absorption apparatus; the other end is closed by a similar stopper, which carries a piece of tubing of very narrow bore, which is connected with the apparatus for drying the oxygen.

The substance to be analysed is contained in a platinum or porcelain boat about 70 mm. long and 8 mm. deep, of such diameter that it slides easily in the combustion tube. It may conveniently be inclosed in a small well-corked tube while being weighed.

The water is absorbed by granulated anhydrous calcium chloride, which is treated with a

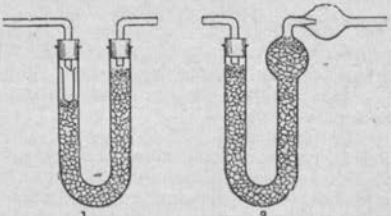


FIG. 17.

current of dry carbon dioxide, and then with a current of dry air to convert any calcium oxide present into carbonate, and thus prevent the absorption of carbonic dioxide.

The calcium chloride is contained in a U-tube provided with a small side bulb for condensing the water, the tube from this bulb fitting directly into the cork in the combustion tube, whilst the other limb of the U-tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle and connected with the potash bulbs (Figs. 18

and 19). In the absence of the side bulb, each limb of the tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle, one of these tubes fitting directly into the cork of the combustion tube, and the other being connected with the potash bulbs. A small test-tube, 2–3 cm. long, placed in the upper part of the first limb of the U-tube, collects the greater part of the water, and thus protects the calcium chloride (No. 1, Fig. 17). (For other forms of calcium chloride tubes, *v.* Chem. Soc. Proc. 1906, 22, 87; Chem. Zeit. 1907, 31, 342.)

A U-tube containing pumice moistened with strong sulphuric acid may also be used to collect the water, but bulbs filled with the acid must not be used, since it dissolves an appreciable quantity of carbon dioxide.

The carbon dioxide is absorbed in a strong solution of potassium hydroxide made by dissolving this substance in an equal quantity of water. The solution is contained in 'potash bulbs,' of which there are many forms. Geissler's form is the most convenient, since it will stand on its own base (No. 2, Fig. 18). Liebig's original form (No. 1) is still used, but the more recent

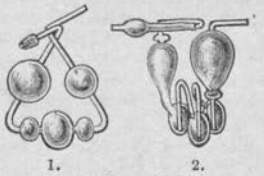


FIG. 18.

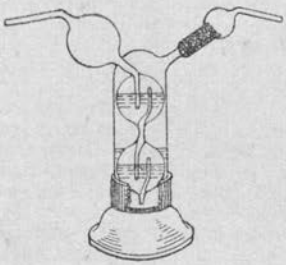


FIG. 19.

form devised by Bender (Fig. 19) secures efficient absorption, and is convenient for weighing, as it stands either on its own base or on an aluminium foot.

The Geissler or Liebig bulbs must contain such a quantity of caustic potash solution that it washes up to a certain extent in the last bulb, but yet is not sufficient to fill the large first bulb in case a vacuum is produced by rapid absorption of the gas. In addition to the potash bulbs, a U-tube filled with granulated soda-lime, with a layer of calcium chloride 2 cm. deep in the upper part of each limb, is used to absorb the last traces of the gas and any small quantity of moisture that may be given off from the caustic potash solution. Two such soda-lime tubes may be used in place of potash bulbs. (For other forms of carbon dioxide absorption tubes, *v.* Chem. Zeit. 1905, 29, 569; 1907, 31, 342; 1908, 32, 77; Amer. Chem. J. 1906, 35, 309; Ann. Chim. anal. 1907, 12, 318; Chem. Soc. Proc. 1908, 24, 182.)

The tube containing the soda-lime is connected with a U-tube filled with calcium chloride, to protect the absorption apparatus from moisture; this is especially needful when the air is drawn through the apparatus by means of an aspirator.

The oxygen or air used in the combustion is freed from carbon dioxide by passing through a strong solution of caustic potash. If compressed oxygen is employed, it is advisable to pass it first through a short length of heated combustion tube containing cupric oxide, in order to burn out any carbonaceous impurity. The air or oxygen is then dried by passing through dry calcium chloride or through pumice moistened with concentrated sulphuric acid, the same desiccating agent must be used to dry the gas as is employed to collect the water produced during the combustion.

The oxygen is dried by passing it through two long U-tubes containing calcium chloride. Instead of the U-tubes we may use a tall cylinder with the lower half filled with soda-lime and the upper with calcium chloride.

The oxygen required for combustions in the open tube may be prepared from potassium chlorate and magnanese dioxide and stored over water in gasholders of moderate capacity. The gas may also be generated as required by the following method, which furnishes the gas under sufficient pressure for use in combustions. A solution of 25 grams of potassium permanganate in 500 c.c. of water, and 50 c.c. of sulphuric acid is introduced drop by drop into a litre flask containing 500 c.c. of hydrogen peroxide (10 vols.). The gas contains chlorine and ozone, which are removed during its passage through the purifiers (Bull. Soc. Chim. 1907, [4] 1, 501).

The operation.—The tube is placed in the furnace and connected at one end with the drying apparatus and at the other with the calcium chloride guard tube, but not with the absorption apparatus. It is gradually heated to redness, a current of dry oxygen is passed through for half an hour to remove all moisture and organic matter, and the tube is allowed to cool. When a combustion tube is being used for the first time or after a long interval, it is advisable to carry out a blank experiment by putting on the absorption apparatus and heating the tube for some time in a stream of dry oxygen. If the tube is ready for the analysis, the weight of the absorption tube and apparatus should be constant. The solid or non-volatile liquid substance is now weighed into the platinum boat, which is introduced into the tube by removing the long copper plug at the back, and the latter is then replaced. The front end of the tube is then connected with the absorption apparatus, and the other end is connected with the drying tubes and the oxygen reservoir. The burners under the front part of the tube are now lighted and the temperature gradually raised until the tube is at a dull-red heat to within 12 cm. of the boat. The tube in contact with the stopper at the front end should be so hot that it can only just be touched by the finger, and this temperature should be maintained throughout the operation by regulating the first two burners, in order to prevent condensation of moisture without decomposing the stopper. If any water should condense, it may be volatilised by bringing

one of the hot tiles close over the tube. The last two or three burners under the long copper plug at the back are now lighted and the temperature gradually raised to dull redness, whilst at the same time the copper oxide is heated to within 5–6 cm. of the boat, and a current of oxygen is passed through the tube at the rate of a bubble every two seconds. One of the burners under the boat is then lighted and the boat very gradually heated, combustion being regulated so that the bubbles passing into the potash bulbs can easily be counted. When the substance is completely carbonised, the temperature of the boat is raised and the current of oxygen increased to a bubble per second. Towards the close of the operation the boat is heated to redness and a somewhat more rapid current of gas is passed. It is not necessary to heat the tube above redness, and a higher temperature produces distortion. When combustion is complete, the current of oxygen is continued for a short time to drive out all carbon dioxide and reoxidise any reduced copper. When the oxygen bubbles through the potash bulbs at the same rate as through the drying apparatus, the oxygen reservoir is disconnected and a current of air is drawn through the whole apparatus to expel the oxygen. At the same time the tube is gradually cooled and is ready for a second operation. If the tube is carefully heated and cooled, it may be used for a very large number of analyses. The absorption apparatus is disconnected and weighed. All the weighings should be made without the plugs of caoutchouc tubing and glass rod which are used to protect the contents of the tubes and bulbs from the air. When several analyses are being made of substances which burn only with difficulty, the entire heating may with advantage be carried out in a current of oxygen, and some saving of time is effected by weighing the absorption apparatus filled with oxygen.

Volatile liquids are inclosed in a small thin cylindrical glass bulb 3 cm. long, with a capillary neck, readily made by drawing out a piece of wider tubing. The bulb is weighed, heated, and the capillary tube immersed beneath the liquid. As the tube cools a small quantity of the liquid enters. This is heated to boiling, and when the air is expelled the end of the tube is again placed in the liquid, and when the vapour condenses the bulb is completely filled. If the liquid is very volatile, the capillary end may be sealed before weighing the tube, but usually this is not necessary. The bulb is placed in the boat with the capillary end open and directed towards the copper oxide. Combustion is conducted as already described, but much greater care is required, especially if the liquid is very volatile. The front part of the copper oxide must be quite red-hot before the liquid begins to volatilise, and it is advisable that the bulb be empty before the copper oxide near the boat is heated. With an iron gutter sufficient heat is conducted to vapourise volatile liquids, but in other cases a very low flame may be used, or one of the hot tiles may be held over the boat. In all cases it is difficult to prevent diffusion of vapour into the back of the tube and even into the drying apparatus. The long copper plug at the back increases the speed of the current by decreasing the diameter of the passage, and the narrow diameter of the entrance tube assists in a similar manner, but in all cases of the analysis of a volatile substance a slow current of air should be passed almost from the beginning. Later, oxygen should be passed, but not too soon, otherwise an explosive mixture may be formed. The open tube, in fact, does not yield such satisfactory results with volatile liquids as with other substances, and in such cases combustion should be made by the following method.

Liebig's original method as modified by Bunsen. Granular cupric oxide and some of the finely divided oxide are heated strongly, and while still hot are placed in flasks with long necks

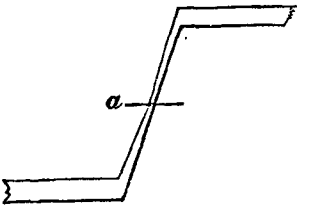


FIG. 20.

which are then tightly corked. The combustion tube is drawn out at one end in the manner shown in the figure, and sealed at the point *a*. A layer of granular cupric oxide about 10 cm. long is first introduced by placing the combustion tube in the neck of the flask (Fig. 21) containing it, and then 2–3 cm. of the finely divided oxide. The substance (about 0·5 gram) is now introduced from a long narrow weighing tube which can be inserted into the mouth of the combustion tube, and 5–6 cm. of the finely divided oxide is added and intimately mixed with the substance by means of a long copper wire, the lower end of which has two twists like a corkscrew (Fig. 22). The wire and sides of the tube are rinsed with some of the oxide, and the tube is filled with the granular oxide to within 5–6 cm. of the top, and a plug of cupric gauze inserted. Every care must be taken to prevent absorption of moisture by the cupric

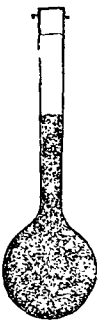


FIG. 21.

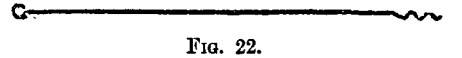


FIG. 22.

oxide. The remainder of the operation is conducted as described above, and when combustion is complete the drawn-out end of the tube is connected with a drying apparatus, the tip broken off inside the caoutchouc tube, and a current of oxygen and afterwards of air passed through the apparatus.

In whichever way the combustion is made it is found that the percentage of hydrogen is always about 0·1–0·15 too high, a result attributed to the difficulty of perfectly drying the cupric oxide, &c. It is frequently stated that an open tube rarely gives correct results the first time it is used; but this is solely due to neglect of the precaution of first heating in a current of oxygen (p. 219).

Combustion with lead chromate. Substances such as graphite, resins, &c. which are oxidised with great difficulty, should be burnt with lead chromate, or in extreme cases with lead chromate containing 10 p.c. of potassium bichromate; these oxidising agents can be employed in either open or closed combustion tubes. The chromate is precipitated by adding potassium bichromate to a solution of lead nitrate, washed, dried, fused, and then granulated. It is heated immediately before being used, and the tube is filled in the same manner as with copper oxide in B. The efficiency of the lead chromate depends mainly on the fact that at a high temperature it fuses. After being used it is heated with nitric acid in order to remove the reduced oxides, and is washed, dried, and again ignited.

Carbon and hydrogen in presence of nitrogen, halogens, &c. When nitrogen is present it is partly converted into nitrogen oxides, which are absorbed by the caustic potash. In order to avoid this source of error, the front of the tube contains plugs of copper wire gauze or a layer of granulated metallic copper 12–15 cm. in length reduced in carbonic oxide. The copper is heated to redness throughout the operation, and the nitrogen oxides are decomposed with absorption of oxygen and liberation of nitrogen. A silver gauze plug is preferable to the copper, because if the latter is reduced in hydrogen, it is apt to retain water, and if in methyl alcohol, it may also contain carbon (Zeitsch. anal. Chem. 1906, 14, 741).

Perkin (Chem. Soc. Proc. 1880, 37, 457) employs precipitated manganic oxide made into a paste with a saturated solution of potassium chromate containing 10 p.c. of dichromate, dried and granulated. A layer of this mixture 15 cm. long is placed in the front of the tube and heated to 200°–250° C. All nitrogen oxides are absorbed, but if the mixture is heated too strongly they are partially expelled. After each analysis the manganic oxide is heated more strongly whilst a current of air is passed through the tube, and the nitrogen oxides are more or less completely driven off.

The halogens, when present, form halide copper salts, which are somewhat volatile and are liable to be carried into the absorption apparatus. In such cases the front layer of copper may be replaced by silver foil or gauze, which decomposes the nitrogen oxides and also absorbs the halogens. Compounds of this kind may also be burnt by means of lead chromate, (*v. supra*), or a mixture of the substance with lead chromate may be placed in a porcelain boat and burnt in a current of oxygen in the usual way (*cf.* Amer. Chem. J. 1906, 35, 531).

Sulphur forms sulphur dioxide, which is absorbed by caustic potash. Compounds containing this element may be burnt with lead chromate, care being taken that the front of the tube is not too hot; or the front of the tube may contain a somewhat longer layer of manganic oxide and potassium chromate, the front half being kept at 200°–250° to absorb nitrogen oxides, whilst the rear half is heated to dull redness and absorbs the sulphur dioxide (Perkin, *l.c.*).

Combustion in presence of a contact substance. The use of a special combustion furnace may be obviated by bringing a mixture of oxygen and the vapour of the organic substance heated to a suitable temperature, into contact with some active material, such as platinum, platinised quartz, platinised asbestos, palladium, or even finely divided copper oxide. This process, which has been applied successfully by Dennstedt and his collaborators to a varied series of organic substances, is carried out in a hard-glass or quartz combustion tube, about 86 cm. in length and 16–18 mm. in diameter, the contact material being placed about the middle of the tube. Platinised quartz is prepared by soaking thoroughly clean and dry quartz fragments in an alcoholic solution of pyridine platinichloride and igniting them over the blow-pipe. A layer of about 3 cm. of this material can be used in the combustion, or platinum foil or wire may be employed, one of the most efficient forms of this metal being a six-rayed star of platinum foil, about 10 cm. in length. The combustion is most conveniently effected in a double supply of oxygen. The boat containing the substance is placed in the hard-glass inner tube (18 cm. in length) shown in Fig. 23, which is open at one end and at the

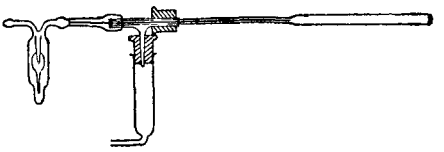


FIG. 23.

other terminated by a wide capillary tube, through which a current of dry oxygen can be introduced. This inner tube has a diameter of about 14 mm., and oxygen can be passed through the annular space by means of the T-tube fitting over the capillary tube as shown in the figure.

By means of this apparatus the supply of oxygen required for vaporising and burning the substance can be carefully regulated. When the organic compound contains nitrogen, sulphur, or halogens, a large boat containing lead peroxide is placed in the combustion tube and heated to 300°–320°. The sulphur is absorbed in the form of lead sulphate, and may be estimated by extracting the lead peroxide with 5 p.c. sodium carbonate solution, and estimating the sulphate in the filtrate. The estimation of chlorine and bromine may be similarly effected. Iodine is not entirely absorbed by lead peroxide, and, accordingly, 'molecular' silver must be employed to take up this element (Dennstedt, Zeitsch. angew. Chem. 1905, 18, 1134; 19, 517; Chem. Zeit. 1905, 29, 52; 1909, 33, 769; Analyst, 1905, 135; Ber. 1908, 41, 600; Baumert, Ber. 1907, 40, 3475). Walker and Blackadder recommend a furnace 60 cm. long, with granular copper oxide partly placed in the combustion tube and partly mixed with the weighed substance. The combustion is carried out in about 30 minutes, and the tube can be heated with Bunsen burners on an ordinary working bench (Chem. News, 1909, 99, 4; *cf.* Marek J. pr. Chem. 1906, 73, 359).

Electrical method. In this process the electric current is used as the source of heat, and platinum as the catalyst. A Dennstedt inner

tube is employed to contain the boat z with the weighed substance, and the spiral of platinum-iridium wire NJ is wound round a porcelain or quartz tube held in position in the combustion tube by a nickel tube DE, passing through the indiarubber stopper C. The coil is heated to redness by the passage of the current through DEJOP, and the absorption apparatus is fitted on to the outer end of the nickel tube DE. A divided stream of oxygen is employed as in the Dennstedt process, and the time required for complete combustion varies from 15 to 40 minutes.

The consumption of electrical energy in

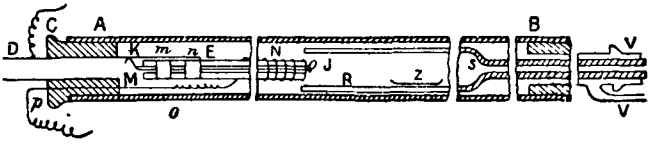


FIG. 24.

this method of carrying out combustions is small, amounting to about 3·6 amperes at 54 volts (194·4 watts) during the time when the highest temperature is obtained (Breteau and Lerona, Bull. Soc. chim. 1908, [4] 3, 15; *cf.* B. Blount, Analyst, 1905, 30, 29; Morse and Taylor, Amer. Chem. J. 1905, 33, 591; Morse and Gray, Amer. Chem. J. 1906, 35, 451; Carrasco and Plancher, Gazz. chim. ital. 1906, 36, 492; Lippmann, Chem. Zeit. 1905, 29, 487, 174; Tucker, J. Amer. Chem. Soc. 1907, 29, 1442).

Nitrogen. This element is determined in the form of ammonia (Will and Varrentrapp, Ruffle, Kjeldahl), or in the form of nitrogen gas, which is collected and measured, the weight being calculated from the volume (Dumas, Maxwell Simpson).

A. *Will and Varrentrapp's method.* The substance is heated with soda-lime and the nitrogen is evolved as ammonia, which is absorbed in hydrochloric acid and precipitated as ammonium platinichloride or estimated volumetrically. This method is not applicable to azo-, diazo-, nitro-, and nitroso- derivatives, and to certain albuminoid substances.

Soda-lime is prepared by slaking 2 parts of good quicklime with a strong solution of 1 part of sodium hydroxide free from nitrates or sulphates. The mixture is dried by heating in an iron vessel, granulated, and preserved in well-closed bottles. A mixture of equal parts of calcium hydroxide and anhydrous sodium carbonate may also be used.

A glass tube about 50 cm. long and 12 mm. diameter, sealed at one end, is filled to a depth of about 5 cm. with a mixture of anhydrous oxalic acid and granular soda-lime, and a short plug of recently ignited asbestos is inserted. The substance is intimately mixed with sufficient finely powdered soda-lime to form a layer about 15 cm. long, and is quickly introduced into the tube. The mortar is rinsed with a small quantity of soda-lime, which is also put in the tube, and the latter is then filled with granular soda-lime to within 5 cm. from the end and a loose asbestos plug inserted. The tube is tapped to form a channel over the powdered soda-lime for the escape of the gases, and is placed in a furnace, which may be considerably shorter than that used in the estimation of hydrogen and oxygen. The combustion tube is attached by means of a perforated cork to an apparatus for absorbing the ammonia. This may consist of the bulbs originally devised by Will and Varrentrapp, or of an ordinary bulb U-tube. Winkler has devised a combination of bulb and flask which is especially convenient for estimations by titration, since the liquid need not be transferred. Ordinary dilute hydrochloric acid or a definite volume of standard acid is placed in the bulb. The tube is gradually heated to redness, beginning at the end near the U-tube, and when decomposition is complete the oxalic acid at the back is heated, and the ammonia in the tube is driven out by the current of carbonic oxide and carbon dioxide. The excess of acid is then determined by standard alkali; or the liquid is evaporated with platinic chloride as in an ordinary estimation of ammonia, and the precipitate is washed with ether containing a small quantity of alcohol, dried, heated in a crucible till completely decomposed, and the nitrogen calculated from the weight of the residual platinum. $Pt=N_2$. The nitrogen frequently forms volatile bases other than ammonia, and hence the platinum precipitate cannot be weighed as such. The ratio of platinum to nitrogen is, however, the same in all cases. The precipitate is washed with ether, because if such bases are present, it may be soluble in alcohol.

It is important that the front part of the tube be heated sufficiently to secure complete decomposition, but the temperature must not be too high, otherwise part of the ammonia itself is decomposed, and the results are too low. Substances rich in nitrogen should be mixed with some pure sugar in order to dilute the ammonia and prevent too rapid absorption.

Various modifications of Will and Varrentrapp's method have been introduced in order to make it more generally applicable, but these processes have been superseded by Kjeldahl's method (*cf.* Ruffle, Chem. Soc. Trans. 1881, 39 87; Arnold, Ber. 1885, 18, 806).

B. *Dumas' method.* In this process the hydrogen and carbon are burnt by means of cupric oxide and the liberated nitrogen collected and measured. A glass tube 80 cm. long, 12 to 15 mm. diameter, sealed like a test-tube at one end, is filled to a length of 12–15 cm. with dry sodium hydrogen carbonate, 4 cm. of cupric oxide is added, and then an intimate mixture of the substance (0·3–0·6 gram) with cupric oxide, then the cupric oxide used to clean the mortar, a layer of granular cupric oxide, and finally a layer of reduced granulated copper or copper-wire gauze not less than 15 cm. in length. The tube is connected by means of a cork and

bent tube with an apparatus for collecting the nitrogen. The sodium hydrogen carbonate is first heated until all air is expelled and the issuing gas is completely absorbed by potash solution. The copper is then heated to redness, the heat being gradually applied to the whole tube as far as the carbonate. When combustion has ceased, the carbonate is again heated until all the nitrogen has been expelled.

The most convenient form of apparatus for collecting the nitrogen is that devised by H. Schiff (Zeitsch. anal. Chem. 7, 430), or a similar form described by Groves (Chem. Soc. Trans. 1880, 37, 500). The former consists of a burette, A, fitted with a heavy foot and provided with a stop-cock, *c*, at the top. Close to the bottom is a tubulus, *b*, inclined at an angle of about 45°, and on the other side is another tubulus, *a*, connected by means of a caoutchouc tube previously soaked in paraffin with a globular reservoir, B, which is attached to the burette by a clip, and the height of which is readily adjusted. Mercury is poured into the burette through the lower tubulus to a height of 2 or 3 mm. above the lower opening, and the reservoir is then filled with a solution of caustic potash in its own weight of water, the lower tubulus being closed with a cork. The stopcock is opened and the reservoir raised until the burette is completely filled with the alkaline solution. The stopcock is then closed and the reservoir lowered to the bottom of the burette. The tubulus may now be opened without the mercury or alkaline solution being forced out. When the air has been expelled from the combustion tube the end of the delivery tube is inserted through the tubulus and the nitrogen collected. At the close of the operation the temperature of the gas is allowed to become constant, the reservoir is raised so that the level of the liquid is the same as in the burette, and the volume of the nitrogen is read off, together with the temperature and the height of the barometer. The weight of the nitrogen, P, is then calculated from the volume by means of the formula

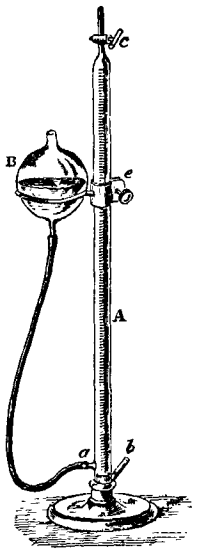


FIG. 25.

$$P = \frac{V(B - f)0{\cdot}001251}{(1 + 0{\cdot}00366t)760},$$

where V is the observed volume, B the height of the barometer, *f* the tension of aqueous vapour at the temperature *t*, and 0·001251 the weight of 1 c.c. of nitrogen at 0° and 760 mm.

Gatterman (Zeitsch. anal. Chem. 24, 57) collects the nitrogen in an apparatus similar to Schiff's, but not graduated. A bent tube of small diameter completely filled with water is attached to the jet of the burette by means of caoutchouc tubing. By closing the lower tubulus, raising the potash reservoir, and opening the stopcock, the gas is driven over into a graduated tube standing over water, and is measured. The error due to the unknown vapour tension of the potash solution is thus avoided, but the vapour tension of the water at the particular temperature must of course be taken into account. Other forms of apparatus are described by Zulkowsky (Annalen, 1876, 182, 296; Roscoe and Schorlemmer's Chemistry, 3, pt. 1, 74) and Schwarz (Ber. 1880, 13, 771).

C. *Maxwell Simpson's modification of Dumas' method* (Chem. Soc. Trans. 1853, 6, 290; Annalen, 1855, 95, 74). In order to avoid the formation of carbonic oxide and nitric oxide, the substance is burnt with a mixture of cupric oxide and mercuric oxide. Into a tube similar to that used in Dumas' method is introduced about 12 grams of manganese carbonate or granulated magnesite mixed with 2 grams of precipitated mercuric oxide, followed by a plug of asbestos. Another gram of mercuric oxide is introduced, and then an intimate mixture of 0·5 gram of the substance with 45 parts of a previously prepared and thoroughly dry mixture of 4 parts of ignited cupric oxide and 5 parts of precipitated mercuric oxide. The mortar and the sides of the tube are rinsed with a similar mixture and another asbestos plug is introduced. A layer of granular cupric oxide about 9 cm. in length and a layer of not less than 20 cm. granulated copper, kept in position by another asbestos plug, fill the remainder of the tube. After the air has been expelled by heating the manganese carbonate or magnesite, the tube is gradually heated to redness, beginning from the front. The metallic copper not only decomposes nitrogen oxides, but also absorbs the excess of oxygen. The gas is collected as in Dumas' method, the magnesite or manganese carbonate providing the carbon dioxide.

Certain organic compounds (*e.g.* hydroaromatic series), when analysed for nitrogen, evolve a portion of their carbon as methane, which, being burnt only imperfectly, adds to the volume of the nitrogen. In these cases lead chromate is recommended as the oxidising agent, or the substance may be mixed with cuprous chloride and copper oxide (Haas, Chem. Soc. Proc. 1906, 22, 81).

Various modifications of Dumas' process have been proposed. Thudichum and Wanklyn use a mixture 5 parts of normal sodium carbonate and 13 parts of fused potassium bichromate in place of sodium hydrogen carbonate. Groves (*l.c.*), with a view to using the same tube repeatedly, places the mixture of carbonate and bichromate in a small tube connected with the combustion tube by an indiarubber joint. The portion of the cupric oxide mixed with the substance is separated from the layer remaining always in the tube by means of a tight plug of asbestos and copper gauze, the latter keeping a free passage for the gas.

The combustion tube may be open at both ends, the rear being connected with an apparatus for generating carbon dioxide, but special precautions must be taken to obtain this gas free from air (*v.* Warington, Chem. Soc. Trans. 1882, 41, 346).

The carbon dioxide required for this modification of Dumas' process may be generated in a Kipp's apparatus by the action of hydrochloric acid on marble or calcite. These minerals should, however, be boiled with water before being used, in order to free them from air. The dioxide may also be generated by dropping a concentrated solution of potassium carbonate (sp.gr. 1·5) into a mixture of water and concentrated sulphuric acid. A convenient apparatus in which to effect this operation is shown in the accompanying figure (Young and Caudwell, J. Soc. Chem. Ind. 1907, 26, 184). The carbonate solution flows from the dropping funnel into the mercury trap and out into the Woulff's bottle through the small hole *a*. The rate of evolution is regulated by the exit tap, and *s* is a safety tube.

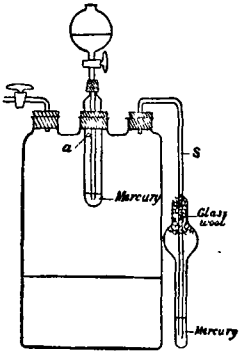


FIG. 26.

In both Dumas' method and Simpson's modification the combustion tube may be drawn out at the front end and connected with a Sprengel mercury pump by glass tubing joined by short pieces of caoutchouc tubing, the joints being surrounded by short wide tubes filled with water or glycerol. A bulb is blown on the horizontal part of the glass tube at the end near the combustion tube, and this bulb is kept cool during the operation, and serves to condense the water which is formed. The combustion tube is made vacuous, and when no more air issues from the end of the pump, the combustion is conducted in the ordinary way, the gas which is evolved being pumped out by the Sprengel pump and collected in a suitable tube. No magnesite need be used. The copper oxide keeps the exhausted tube from collapsing when heated.

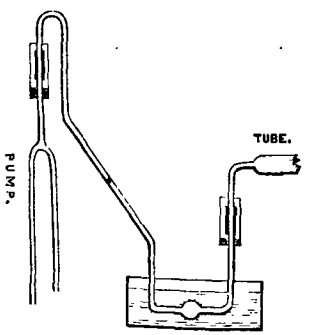


FIG. 27.

In many cases, especially with nitro- derivatives, the gas generated in the exhausted tube is a mixture of nitrogen with nitric oxide, the latter being sometimes present in considerable quantity. It is advisable, therefore, to decompose the nitric oxide by using either a layer of reduced copper or a long plug of silver gauze placed between the copper oxide and the exit, and by keeping this material heated throughout the combustion.

Liquids in which nitrogen is to be determined may be enclosed in bulbs which are dropped into the combustion tubes as in the determination of hydrogen and oxygen.

The copper oxide used in nitrogen determinations should be prepared by heating metallic copper in air and never by ignition of the nitrate, since in the latter case it is apt to contain basic nitrates which evolve nitrogen on heating.

The copper used in nitrogen determinations, &c., should not be reduced in hydrogen, since it is liable to occlude this gas. It may be reduced in the mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with strong sulphuric acid. Plugs of copper gauze may also be reduced by heating them to redness and dropping them into a test-tube containing a few drops of formic acid or methyl alcohol. The reduced copper is carefully dried at 100°–110°.

When no carbonate is used and the gas is simply pumped out of the tube and collected over mercury, it consists of a mixture of carbon dioxide and nitrogen. If the former is estimated by absorption with caustic potash, a determination of the carbon may be combined with that of nitrogen.

Jannasch and Meyer have described a method for the simultaneous estimation of carbon, hydrogen, and nitrogen (Ber. 1886, 19, 949; Annalen, 1886, 233, 375; Zeitsch. anal. Chem. 1887, 26, 86; *cf.* Bull. Soc. chim. 1905, 33, 951).

D. *Kjeldahl's method* (Zeitsch. anal. Chem. 1883, 22, 366). The substance is heated with concentrated sulphuric acid to a temperature approaching the boiling-point of the latter, and when decomposition is complete, an excess of solid potassium permanganate is added. The nitrogen is thus converted into ammonium sulphate, which is then distilled with excess of alkali and the ammonia collected and estimated. This method is economical, requires no combustion furnace or special apparatus, is rapid, and requires comparatively little attention, so that a large number of determinations can be carried on at the same time. The substance need not be in a very fine state of division, and the method is especially suitable for liquid and pasty substances such as extracts.

It is important that the sulphuric acid employed for these determinations should be protected from ammonia, and the caustic soda solution should be well boiled in order to expel any ammonia which it may contain. The purity of the reagents is best ascertained by making an experiment with pure sugar. If a small quantity of ammonia is present, the same quantity of the reagents should be used in each experiment, and a correction made for the ammonia which they contain.

In order to prevent bumping during distillation.

a small piece of zinc may be placed in the flask, but it is essential that the soda should be free from nitrates and nitrites, which would be reduced and yield ammonia.

The time required for the operation may be considerably shortened by using sulphuric acid containing sulphuric anhydride or phosphoric anhydride.

The method as thus carried out is applicable to all substances which can be analysed by Will and Varrentrapp's process, and to many others.

Heffter, Hollrung, and Morgen (Zeitsch. f. Chem. 8, 432) treat 1·0–1·5 grams of substance with 20 c.c. of a mixture of 4 vols. ordinary sulphuric acid and 1 vol. of fuming acid, and 2 grams of phosphorus pentoxide. Kreusler (Zeitsch. anal. Chem. 1885, 24, 453) uses sulphuric acid containing 200 grams of phosphorus pentoxide per litre.

Wilfarth (Chem. Zentr. [3] 16, 17, 113) finds that the oxidation of the organic matter takes place much more rapidly in presence of certain metallic oxides. Mercuric oxide is the most efficient, but cupric oxide answers almost equally well. The former produces mercuri-ammonium derivatives, which are not readily decomposed by caustic soda, and hence the alkaline liquid must be mixed with some potassium sulphide to decompose the mercury compounds. The mercuric sulphide formed makes the liquid boil regularly without the addition of zinc. Ulsch recommends the use of ferrous sulphate instead of potassium sulphide; it may be added before the caustic soda.

Warington (Chem. News, 1885, 52, 162) removes nitrites and nitrates by boiling with ferrous sulphate and hydrochloric acid.

With a view to secure the reduction of nitro-derivatives, &c., and thus make the process generally applicable, Asboth (Chem. Zentr. [3] 17, 161) mixes 0·5 gram of the substance with 1 gram of pure sugar in the case of readily oxidisable compounds, and with 2 grams of benzoic acid in the case of nitrates and similar derivatives. Most probably the benzoic acid first forms nitro- derivatives, which are afterwards reduced. He adds Rochelle salt with the caustic soda in order to prevent precipitation of manganese, &c., and thus avoids bumping during distillation. With these modifications the method is applicable to all nitrogen compounds except those of the pyridine and quinoline series. E. Arnold (*ib.* p. 337) uses 0·5 gram of anhydrous cupric sulphate and 1 gram of metallic mercury in place of the oxides as recommended by Wilfarth, and heats 1 gram of the substance with these and 20 c.c of sulphuric acid containing 20–25 p.c. of phosphoric oxide.

C. Arnold (Arch. Pharm. [3] 24, 785) confirms Asboth's statements, but finds that in addition to pyridine and quinoline compounds, azo- derivatives and nitrites yield unsatisfactory results. He heats 0·5 gram of substance with 0·5 gram of anhydrous cupric sulphate, 1 gram of metallic mercury, 2 grams of phosphoric oxide, 1 gram of sugar, and in case of nitrates, &c., 2 grams of benzoic acid, and 20 c.c. of sulphuric acid.

Reitmair and Stutzer (Rep. Anal. Chem. 5, 232; Zeitsch. anal. Chem. 1886, 25, 582) use about 0·7 gram of mercuric oxide and 20 c.c of sulphuric acid, with a small fragment of paraffin in the case of substances rich in fat. They regard the use of phosphoric oxide as unnecessary, and the use of fuming sulphuric acid as undesirable on account of its liability to contain nitrogen oxides.

Jodlbauer (Chem. Zentr. [3] 17, 433) uses phenolsulphonic acid in place of benzoic acid, and reduces with zinc dust. He thus obtains good results even with nitrates. Reitmair and Stutzer (Rep. Anal. Chem. 7, 4) find that the nitrate must be somewhat finely divided; 0·5 to 1·0 gram of the substance is mixed with 50 c.c. of sulphuric acid containing 20 grams of phenol per litre, allowed to stand for a short time with occasional agitation, mixed with 2–3 grams of dry zinc powder and 1 or 2 drops of metallic mercury, and heated in the usual way. Conversion into ammonium sulphate requires one and a half hours.

A most important improvement in the Kjeldahl process due to Gunning (Zeitsch. anal. Chem. 28, 188), consists in the addition of potassium sulphate to the concentrated sulphuric acid. The solution of potassium hydrogen sulphate in concentrated sulphuric acid boils at a temperature considerably above the boiling-point of the strong acid and the oxidation of the organic matter is thereby greatly facilitated. Various oxidising and catalytic agents may be employed in conjunction with this mixture, and the following are among the many which have been suggested in addition to those already mentioned: platinic chloride, ferric chloride, manganese dioxide, magnesia, and sodium phosphate. The use of potassium permanganate has now been abandoned, and, in the case of refractory substances, oxidation is now generally induced by the catalytic action of mercury or its oxide. The following process is described by Dyer (Chem. Soc. Trans. 1895, 67, 811). The substance (0·5–5 grams) is introduced into a round-bottomed Jena flask, and heated gently with 20 c.c. of concentrated sulphuric acid containing a small globule of mercury. After the initial action has subsided, the temperature is raised to boiling, and in 15 minutes 10 grams of potassium sulphate are added, and the boiling continued till the solution is clear and colourless. The flask is closed with a loosely fitting bulb stopper, from the internal projection of which the condensed sulphuric acid drops back into the flask. There is, therefore, little loss of acid except through reduction to sulphurous acid. The product is rinsed into a capacious Jena distilling flask, rendered strongly alkaline with sodium hydroxide, with the addition of a small quantity of sodium sulphide, and the liquid distilled in a current of steam, the ammonia being collected and estimated in the usual way.

When nitrates are present, Jodlbauer's modification is employed, but the phenol may conveniently be replaced by salicylic acid. When the solution of this substance in concentrated sulphuric acid is poured quickly on to the weighed material, the loss due to the formation of lower oxides of nitrogen is avoided, and satisfactory results are obtained even when ammonium nitrate is present. This circumstance is of great importance in connection with the analysis of compound fertilisers containing both ammonium salts and alkali nitrates. The

zinc and mercury are added while the solution is still cold, and the former metal allowed to dissolve before the mixture is heated. Other reducing agents, such as sugar and sodium thiosulphate, may be used either alone or in conjunction with zinc. By the aid of this modified process satisfactory results are obtained in the analysis of organic nitro-,azo-,and hydrazo-derivatives. It has not been found possible to obtain correct estimations of nitrogen in sodium nitroprusside, phenylhydrazine and its derivatives, and in mixtures containing large proportions of chlorides and nitrates (*cf.* J. Amer. Chem. Soc. 17, 567; Analyst, 1905, 314; Ber. 1905, 38, 559; Chem. Soc. Proc. 1901, 25, 351; 1903, 27, 988).

The literature of nitrogen determinations is extremely voluminous. Summaries of contributions to this subject will be found in Zeitsch. anal. Chem. 1884, 23, 551; 24, 439; 25, 424 and 571; 26, 249; and Chem. News, 1888, 57, 62, *et seq.* In addition to the references already given, papers relating to Kjeldahl's process may be found in Zeitsch. anal. Chem. 24, 199, 388, and 393; 25, 149 and 155; 26, 92; 27, 222 and 398.

Chlorine, bromine, and iodine.

By lime. A tube about 40 cm. long and 7 mm. diameter, sealed at one end like a test-tube, is filled to a depth of 5 cm. with pure granulated quicklime. The substance is weighed into the tube and mixed with finely powdered lime by means of a copper wire twisted at the end like a corkscrew. The wire and tube are rinsed with lime, the tube is filled to within 5 cm. of the open end with granulated lime. The tube is gradually heated to redness from the front. When cold the contents of the tube are dissolved in water slightly acidified with nitric acid, filtered, and the halogen precipitated by silver nitrate.

In the case of iodine the substance is dissolved in water, filtered, mixed with silver nitrate, and finally acidified, in order to avoid liberation of iodine. A further precaution consists in adding a little sodium sulphite before each addition of nitric acid.

When the substance contains nitrogen, cyanides may be formed; but this is avoided by using pure soda-lime in place of lime. If the lime contains sulphates, some sulphide is liable to be produced. (On the preparation of pure lime, *see* Zeitsch. anal. Chem. 4, 51 and 15, 5.)

Liquids are contained in small bulbs with capillary openings, which are dropped into the tube before filling up with lime. The tube must be very gradually heated, and should be longer than usual.

Carius's method (Annalen, 1860, 116, 1; 1865, 136, 129; Ber. 1870, 3, 697). The substance is oxidised by heating with nitric acid in sealed tubes in presence of silver nitrate. In many cases acid of sp.gr. 1·2 and a temperature of 120°–200° will suffice; but substances which are more difficult to oxidise require acid of sp.gr. 1·42, mixed in special cases with some potassium dichromate, or the fuming acid of sp.gr. 1·5 may be used. If necessary the tubes may be heated as high as 300°. The quantity of acid used should not be more than twice that theoretically required for complete oxidation, and the tube must not contain more than 4 grams of nitric acid for each 50 c.c. of its volume. If the operation is prolonged, it is desirable to reduce the pressure in the tube by opening it from time to time by heating the capillary end of the previously cooled tube in a flame until it softens, when the gas forces its way out.

The weighed substance is enclosed in a narrow tube of thin glass of such length that its mouth projects above the nitric acid in the tube, and the acid does not come in contact with the substance until the tube is sealed. The tubes used should be about 15 mm. in diameter and 1·5–2 mm. thick in the glass. After introduction of the substance they are drawn out to a capillary tube with thick walls, which is then sealed. The sealed tubes are heated in a pressure tube furnace tilted at one end so that the capillary ends of the tubes do not come into contact with the liquid. After being heated, the tubes should on no account be removed from the protecting iron or steel tube until they have been opened. For this purpose the tubes are held in position by means of a cork collar through which the capillary ends project out of the furnace. The capillary end is first gently warmed to volatilise any condensed acid, and then heated more strongly until the gases under pressure blow a hole through the softened tip of the sealed capillary. In this operation the pressure of the imprisoned gases is very great, and it is extremely dangerous to attempt to open the tube with a file. The tube furnace should only be used for this purpose within a well-protected enclosure (Fig. 28), so as to minimise the personal risks arising from explosions of the heated tubes.

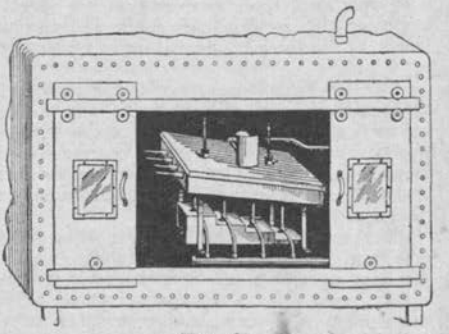


FIG. 28.

The silver salt formed is rinsed out of the opened tube and treated in the usual way.

For the estimation of iodine in organic compounds this method is to be preferred to the lime process, but as the silver nitrate and silver iodide frequently form a fused yellow mass, the mixture must be extracted thoroughly with hot water in order to remove the former salt. The silver halide obtained by the Carius method is collected in a tared Gooch crucible, washed successively with water and alcohol, dried at 100°, and weighed.

Stepanow's method. The substance is boiled with alcohol (20–40 c.c.) and sodium is added at such a rate that a vigorous reaction is maintained. A large excess of the metal is essential

$$XCl + 2Na + C_2H_5{\cdot}OH = XH + NaCl + C_2H_5{\cdot}ONa.$$

When all the sodium has dissolved, 20–40 c.c. of water are added, and the alcohol removed by distillation. The aqueous solution is acidified with nitric acid, and the halogen estimated gravimetrically, or volumetrically by Volhard's method (Ber. 1906, 39, 4056; cf. Bacon, J. Amer. Chem. Soc. 1909, 31, 49). By using the latter method and weighing the mixed silver halides, the two halogens can be estimated indirectly in the same compound.

Pringsheim's method consists in burning the organic substance with sodium peroxide. Compounds containing more than 75 p.c. of carbon are mixed with 18 parts of this oxidising agent, and those with 50–75 p.c. of carbon with 16 parts. Substances containing less than 25 p.c. of carbon are mixed with sugar or naphthalene, and treated with 16–18 parts of the peroxide. The mixture is placed in a steel crucible surrounded by water and having a perforated lid through which a glowing iron wire is thrust to cause ignition. The product is extracted with water, acidified with nitric acid, and the halogen estimated in the usual way (Ber. 1903, 36, 4244; 1904, 37, 324; 1905, 38, 2459; Amer. Chem. J. 1904, 31, 386; *cf.* Moir, Chem. Soc. Proc. 1907, 23, 233; Baubigny, Bull. Soc. chim. 1908, (iv.) 3, 630).

Sulphur and phosphorus.

Non-volatile substances. Pure caustic potash is fused in a silver dish with about one-sixth its weight of potassium nitrate and a little water. When cold the substance is weighed into the dish, which is again heated, the substance being mixed with the alkali by means of a silver spatula. When oxidation is complete, the mass is allowed to cool, and is then dissolved in water acidified with hydrochloric acid, and the sulphuric or phosphoric acid estimated in the usual way.

Carius's method is carried out exactly as in the estimation of the halogens. Sulphur is oxidised to sulphuric acid and phosphorus to phosphoric acid. It is advisable to remove the greater part of the nitric acid before precipitating barium sulphate or magnesium ammonium phosphate.

Another method applicable to volatile and non-volatile substances is as follows:—Into a combustion tube 40 cm. long, sealed at one end, is introduced 2–3 grams of pure mercuric oxide, then a mixture of the substance with equal proportions of mercuric oxide and pure anhydrous sodium carbonate, and the remainder of the tube is filled with sodium carbonate mixed with a small quantity of mercuric oxide. The open end of the tube is closed by a cork carrying a glass tube dipping under water, in which the mercury is condensed. The tube is carefully heated so that the front layer of sodium carbonate is red hot before the substance begins to volatilise. The substance is then rapidly heated, so that decomposition is complete in about fifteen minutes, and finally the mercuric oxide at the rear end of the tube is heated until oxygen issues from the end of the delivery-tube (Russell, Chem. Soc. Trans. 1854, 7, 212; J. pr. Chem. 1855, 64, 230). The contents of the cooled tube are dissolved in water, a small quantity of bromine water added to oxidise any sulphide, the solution acidified with hydrochloric acid, boiled to expel bromine, and the sulphuric acid or phosphoric acid estimated in the usual way.

Many non-volatile substances may be oxidised by heating with pure concentrated caustic potash solution, diluting with twice the volume of water, and treating with a current of chlorine. After complete oxidation the solution is acidified, heated to expel chlorine, and the sulphuric or phosphoric acid determined.

Arsenic. The estimation of this element in organic compounds has recently acquired increased importance owing to the application of these substances in therapeutics. One of the earliest methods, due to La Coste and Michaelis (Annalen, 1880, 201, 224), consisted in mixing the substance with soda-lime, and heating the mixture in a stream of air or oxygen. The residue was dissolved in nitric or hydrochloric acid, the arsenic precipitated as sulphide, and afterwards converted into magnesium pyroarsenate. Monthoulé recommends destroying the organic matter with nitric acid containing magnesium nitrate, when a final ignition leads to the formation of magnesium arsenate (Ann. Chim. anal. 1904, 9, 308).

Pringsheim oxidises the organic arsenic derivative with sodium peroxide, and estimates the arsenic as magnesium pyroarsenate (Amer. Chem. J., 1904, 31, 386).

The following procedure has been shown to be applicable to the organic arsenical drugs now on the market. The substance (0·2–0·3 gram) is mixed with 10–15 grams of sodium peroxide and sodium carbonate in equal proportions, the mixture heated gently in a nickel crucible for 15 minutes, and the temperature then raised to dull redness for 5 minutes. The product is extracted with water, 25–31 c.c. of sulphuric acid (1 : 1) added, and the solution concentrated to 100 c.c., when 1 gram of potassium iodide is added and the liquid boiled down to 40 c.c. After destroying any trace of iodine with a few drops of sulphurous acid, the solution is diluted considerably with hot water, and the arsenic precipitated as sulphide. The precipitate, after washing three times with hot water, is dissolved with 20 c.c. of *N*/2-sodium hydroxide, and the filtered solution treated with 30 c.c. of hydrogen peroxide (20 vols.), the excess of this reagent being destroyed by heating on the water-bath. A few drops of phenolphthaleïn are added followed successively by 11 c.c. of sulphuric acid (1 : 1) and one gram of potassium iodide; the solution is evaporated down to 40 c.c. and the pale-yellow colour removed by sulphurous acid. Cold water is then added, and the diluted solution neutralised with 2*N*-sodium hydroxide, and just acidified with sulphuric acid. The arsenite solution is now titrated with standard iodine solution and starch in the presence of sodium hydrogen carbonate or sodium phosphate (Little, Cahen, and Morgan, Chem. Soc. Trans. 1909, 95, 1477).

Antimony. When present in organic compounds, this element may be estimated by acidifying the product of the sodium peroxide fusion (*v. Arsenic, supra*), and precipitating as sulphide, this precipitate being collected, washed, and weighed in the manner indicated under *Gravimetric determinations.*

Oxygen. No satisfactory method has yet been devised for the direct determination of this

element, and it is usually estimated by difference (*v.* v. Baumhauer, Annalen, 90, 228; Zeitsch. anal. Chem. 5, 141; Stromeyer, Annalen, 117, 217; Mitscherlich, Zeitsch. anal. Chem. 6, 136; 7, 272; 13, 74, and 15, 371; Ladenburg, Annalen, 135, 1; Maumené, Compt. rend. 55, 432; and Cretin, Zeitsch. anal. Chem. 13, 1).

Proximate analysis of carbon compounds.

The methods to be adopted for the separation of the constituents of any particular mixture will depend entirely upon the nature of the mixture. It is only possible to describe the general methods which are found to be most useful in organic analysis. To a certain limited extent these operations are applicable to the proximate analysis of complex inorganic mixtures.

Fractional distillation is available for the separation of liquids which differ considerably in their boiling points (*v.* DISTILLATION).

Distillation in a current of steam is frequently employed as a method of proximate analysis. In this way volatile organic acids can be separated from volatile bases by steam-distilling the mixture in the presence of mineral acids. On the other hand, volatile bases are separated from organic acids by distilling in steam the mixture of these substances rendered alkaline by sodium or potassium hydroxide.

Fractional precipitation may be employed for the separation of substances, some of which are precipitated by a given reagent, whilst the others are not; or for the separation of substances which differ in the *order* of their precipitation. If, for example, silver nitrate is added in successive small quantities to a solution containing an iodide, bromide, and chloride, the first portion of the precipitate contains the greater part of the iodine; the middle portion contains the greater part of the bromine; and the last portion the greater part of the chlorine. In a similar manner organic acids can, not unfrequently, be separated by taking advantage of differences in the order of their precipitation by silver nitrate or lead acetate. In these cases the separated precipitates can be suspended in water and decomposed by hydrogen sulphide, when the acids are again liberated.

Fractional crystallisation may be adopted in the case of substances which differ in their solubility in one and the same solvent. The solution is concentrated somewhat, and the crystals which separate are removed; the mother liquor is still further concentrated, and the second crop of crystals is removed, this process being repeated as often as the case demands. The least soluble compound is mainly in the first crop of crystals; the most soluble is in the last mother liquor.

Fractional saturation is an analogous process, but is of more limited application. It was employed by Liebig for the separation of volatile organic acids. The mixture of acids is mixed with a quantity of caustic soda or potash insufficient for complete saturation, and is then distilled. The acids of higher molecular weight are first neutralised and converted into salts, which of course remain in the retort, whilst the acids of lower molecular weight are found in the free state in the distillate. Anything like complete separation is only to be obtained by many repetitions of this process.

Fractional solution.—The most useful and most generally applicable method of proximate analysis is based upon the different solubilities of various substances in different *menstrua*. The mixture is treated successively with various solvents, each of which dissolves some of the constituents, but leaves the others undissolved. Advantage may also be taken of the fact that the solubilities are in many cases modified by a rise of temperature. Further, if two substances differ considerably in their solubility in one and the same liquid, they may be separated by treatment with successive small quantities of the liquid, which removes the more soluble compound but leaves the greater part of the other undissolved. The following is a list of the solvents commonly employed, with indications as to their general properties:—

Water dissolves many salts and acids; inorganic and organic alkalis and their salts; carbohydrates, gums, certain alcohols, polyhydric phenols, and other highly oxidised carbon compounds which are not readily soluble in alcohol, ether, &c. On the other hand, it does not dissolve the carbonates, phosphates, oxalates, and certain other salts of the heavier metals. Very many organic substances are insoluble in this liquid. It decomposes the halogen compounds of the acid radicles and certain other compounds, and converts many normal metallic salts into basic salts, part of the acid passing into solution in the free state.

Dilute acids will dissolve many salts, and also some organic substances which are insoluble in water.

Alcohol dissolves many salts, caustic alkalis, hydrocarbons, fatty acids, resins, and a very large number of carbon compounds. It reacts with many haloid substitution derivatives, and hence is not a suitable solvent for this class of compounds.

Ether dissolves a few salts, and is an excellent solvent for hydrocarbons, fats, resins, alkaloids, and almost all organic compounds which are insoluble in water. It reacts with very few substances, and boils at a low temperature, so that it can readily be distilled off and the dissolved substance recovered.

Benzene dissolves iodine, sulphur, phosphorus, oils, fats, wax, camphor, resins, caoutchouc, gutta-percha, &c., and is especially useful as a solvent for haloid derivatives, on which it has no action. In certain instances this hydrocarbon may be replaced by its homologues, toluene, and the xylenes.

Carbon disulphide shares with ether the advantage of being readily volatile. It should always be purified from dissolved sulphur before being used. The best plan is to mix it with a small quantity of white wax, and then distil off the disulphide on a water-bath. It dissolves sulphur, phosphorus, iodine, fats, essential oils, resins, caoutchouc, &c.; but its solvent powers are comparatively limited, and almost all salts and very many carbon compounds are insoluble in it.

Light petroleum consists of the more volatile hydrocarbons of the paraffin series. It occurs in commerce in several varieties under different names. *Petroleum ether* boils at 50°–60°; *petroleum benzene*, at 70°–90°; *ligroïn*, at 90°–120°. They are excellent solvents for oils and fats, but

dissolve very few other compounds. Three grades of light petroleum are now obtainable for use as solvents, boiling respectively at 40°–60°, 60°–80°, and 80°–100°.

Chloroform readily dissolves oils, fats, and similar substances, and is especially useful as a solvent for alkaloids.

The chloro- derivatives of ethane and ethylene have been introduced as useful non-inflammable solvents for oils, fats, or resins; these liquids give a wide range of boiling-points and solvent action (Koller, 7th Congress Applied Chemistry, 1909). A large number of other solvents are applied in certain special cases, and among those more commonly employed may be mentioned, acetone, ethyl acetate, amyl alcohol, pyridine, aniline, and nitrobenzene.

The treatment of a solid with a volatile solvent must be conducted in a special apparatus, especially if the liquid is to be heated. Various forms of apparatus have been devised for this purpose, but there is none more efficient than that of Soxhlet (Dingl. poly. J. 232, 461). It consists of a short wide test tube (E), open at the top but closed at the bottom, to which is sealed a narrower tube (N) which can be fitted

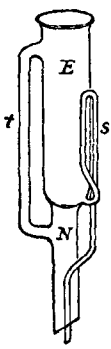


FIG. 29.

FIG. 30.

into a small weighed flask by means of a cork. Communication between the two tubes is made by means of (1) a narrow side tube (*s*) which opens into the bottom of the wider upper tube, forms a siphon, and descends through the lower tube nearly to the bottom of the flask; and (2) a wider side tube (*t*) which enters the upper tube near the top and the lower tube near the junction (Fig. 29). A weighed quantity of the substance to be treated is placed in a cylinder of filter paper open at the top, and introduced into the upper tube, or the bottom of the tube is packed with purified cotton wool, and the substance is placed upon this. A quantity of the solvent rather more than sufficient to fill the upper tube to the level of the bend in the siphon, is placed in the flask and heated to boiling by means of a water-bath. The upper tube is attached to a reflux condenser, care being taken that the condensed liquid falls directly into the cylinder containing the substance. The vapour passes up the wide side tube, is condensed, falls upon the substance, and filters through the paper or cotton wool. As soon as the liquid rises to the bend of the siphon, the latter draws off the clear solution into the flask, and the liquid is again volatilised whilst the dissolved matter remains in the flask. The process goes on automatically, and the substance can be extracted many times with a small quantity of liquid. When extraction is complete, the flask is connected with an ordinary condenser, the liquid is distilled off, and the residue dried and weighed if necessary.

A convenient apparatus for treatment with solvents in dishes has been described by A. W. Blyth (Chem. Soc. Trans. 1880, 37, 140).

In many cases substances in solution can be removed and separated by agitating the liquid with some non-miscible solvent. The alkaloids and many amines can be removed from aqueous solutions by means of ether, whilst metallic salts are left; fatty substances can be removed from liquids by means of light petroleum, and so on. Extractions of this kind are best made in a separator consisting of a somewhat wide tube contracted at one end, which is fitted with a cork or stopper, whilst the other end is drawn out into a narrow tube provided either with a stop-cock or an indiarubber tube and a pinch-cock (Fig. 30). The liquid and the solvent can be completely mixed by agitation, and after they have separated the lower layer can be drawn off. If it is required to remove the supernatant liquid in this or any similar case, a somewhat narrow tube is bent twice at right angles, and one limb is fitted by means of a cork into a distilling or other flask, which is connected with an aspirator, whilst the other limb of the tube is placed in the liquid. When the aspirator is set in action, the liquid is drawn over into the flask, from which it can be distilled. With care a very accurate separation can be made, and the tube is readily rinsed by drawing some of the fresh solvent through it. This method may be rendered approximately quantitative by calibrating the above cylindrical separator (Fig. 30).

The microscope is of the greatest service in ascertaining whether a substance is a single compound or a mixture, and a microscopic examination of the various products obtained in the course of a proximate analysis affords valuable information as to the extent to which separation has been effected.

ESTIMATION OF RADICLES COMMONLY OCCURRING IN ORGANIC COMPOUNDS.

In this section it is only possible to indicate briefly a few of the most general methods by which certain typical radicles present in organic compounds can be estimated.

Hydroxyl. A known weight of the hydroxylic compound is treated with excess of magnesium methyl iodide (Grignard's reagent), and the amount of methane evolved is measured in a gas burette (Fig. 31).

$$R{\cdot}OH + CH_3{\cdot}MgI = R{\cdot}OMgI + CH_4.$$

The organic magnesium compound is dissolved in dry amyl ether or phenetole, and if the hydroxylic compound is too insoluble in either of these solvents, it may be dissolved indry pyridine. (Hibbert and Sudborough, Chem. Soc. Trans. 1904, 85, 933; and Zerewitinoff, Ber. 1907, 40, 2023.)

This process has been extended to the estimation of sulphydryl- (SH), imino-, and

amino- groups, and for all active hydrogen atoms (*cf.* Ber. 1908, 41, 2233 and 3025).

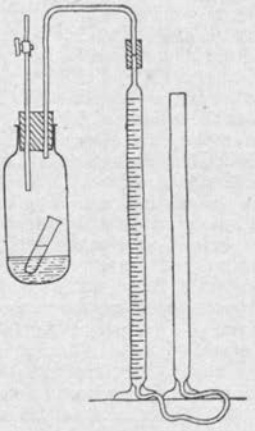


FIG. 31.

Methoxyl.

The estimation of methoxyl, a radicle present in many naturally occurring organic compounds, is generally accomplished by Zeisel's method, which consists in heating the substance with concentrated hydriodic acid or with a mixture of this acid and acetic anhydride. Methyl iodide is evolved and absorbed in alcoholic silver nitrate, with the result that silver iodide is precipitated, each molecular proportion of this substance being equivalent to one

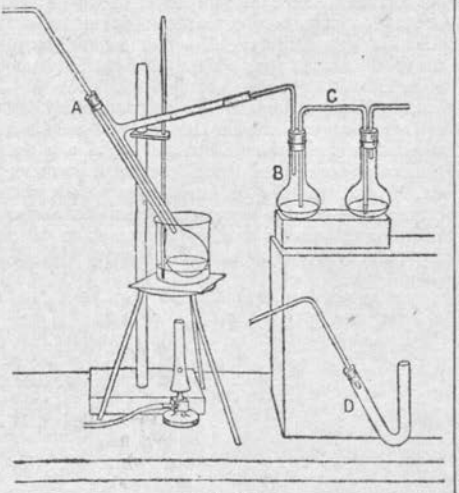


FIG. 32.

methoxyl group. Zeisel's original apparatus (Monatsh. 1885, 6, 989; 1886, 7, 406) has been modified subsequently by several investigators (M. Bamberger, Monatsh. 1894, 15, 904; Perkin, Chem Soc. Trans. 1903, 83, 1367; Hesse, Ber. 1906, 39, 1142; Decher, Ber. 1903, 36, 2895; Hewitt and Moore, Chem. Soc. Trans. 1902, 81, 318). Of these modifications Perkin's (Fig. 32) is probably the simplest; it consists of a distilling flask, A, with a very long neck (20–25 cm.) heated in a glycerine bath at 130°–140°, a current of carbon dioxide being passed through the mixture of substance and concentrated hydriodic acid. The heating is continued for one hour, and the temperature finally raised, so that the hydriodic acid boils gently, but without distilling into the side tube of the distilling flask. The methyl iodide is collected in two flasks, B, containing alcoholic silver nitrate. The precipitated silver iodide is treated with nitric acid, the alcohol evaporated, and the precipitate collected and weighed in the usual manner.

Zeisel's method and its modifications are applicable to the estimation of ethoxyl, but the results obtained are generally less accurate.

Methyl.

A further modification of Zeisel's method renders it available for the estimation of methyl groups attached to nitrogen. The substance is heated with concentrated hydriodic acid and dry ammonium iodide, and the methyl iodide evolved dealt with in the manner indicated above (Herzig and H. Meyer, Ber. 1894, 37, 319; Monatsh. 1894, 15, 613; 1895, 16, 599; 1897, 18, 379; Kirpal, Ber. 1908, 41, 820).

Acetyl.

It is only possible in comparatively few cases to determine with certainty by ultimate analysis the number of acetyl groups existing in organic compounds. For example, the mono-, di-, and tri- acetyl derivatives of the trihydroxybenzenes have approximately the same percentage composition. These and other similar acetyl derivates are hydrolysable by standard caustic alkalis employed in alcoholic solutions, even when they are not readily attacked in aqueous solutions (Benedikt and Ulzer, Monatsh. 1887, 8, 41; Van Romburgh, Rec. trav. chim. 1882, 1, 48; R. Meyer and Hartmann, Ber. 1905, 38, 3956). Acid hydrolysis may be employed in a large number of cases and the volatile acetic acid distilled into standard alkali, the excess of which is determined by alkalimetry. According to Wenzel's process, the acetyl derivative is first hydrolysed by moderately strong sulphuric acid ($1 : 2H_2O$), and the mixture treated with monosodium phosphate and boiled down to dryness; the sulphuric acid is fixed as sodium sulphate, and the acetic acid is distilled into a known excess of standard alkali, the distillation being carried out under reduced pressure (Monatsh. 1893, 14, 478; 1897, 18, 659).

The destructive action of strong sulphuric acid on organic compounds may be avoided by the use of the aromatic sulphonic acids as hydrolytic agents. The acetyl compound is distilled in steam in a 10 p.c. solution of benzenesulphonic acid or one of the naphthalenesulphonic acids; the distillate, which contains all the acetic acid furnished by the hydrolysis, is titrated with standard barium hydroxide (Sudborough and Thomas, Chem. Soc. Trans. 1905, 87, 1752).

A. G. Perkin hydrolyses the acetyl compound with alcoholic sulphuric acid, adding fresh alcohol from time to time. The ethyl acetate obtained in the distillate is then hydrolysed with a known amount of standard caustic alkali, and the excess of the latter ascertained with standard acid (Chem. Soc. Trans. 1904, 85, 1462; 1905, 87, 107; 1907, 91, 1230).

Carboxyl.

In many cases the number of carboxyl (CO_2H) groups in an organic compound can be determined by the analysis of its neutral salts. For this purpose the silver salts are generally selected, as they are usually anhydrous, and indicate the normal basicity of the organic acid. The aromatic hydroxy-carboxylic acids (*e.g.* 1 : 5-dinitro-*p*-hydroxybenzoic acid) take up two atoms of silver, one replacing the carboxylic, and the other the phenolic hydrogen. Some silver salts of organic acids are sensitive to light, and others are very explosive. The more stable ones can be analysed by direct ignition and weighing the residual silver. In other cases the organic matter must be destroyed with nitric acid, and the silver estimated as chloride in the acid liquid.

Other metallic salts are frequently employed in determining the basicity of carboxylic acids, and it is advisable before arriving at a final conclusion to estimate the metals in a series of these compounds.

If the molecular weight of a carboxylic acid is known, the basicity can often be determined by titration with aqueous or alcoholic sodium, potassium, or barium hydroxide; the indicators generally employed are phenolphthaleïn, methyl orange, and lacmoid.

The following indirect method has been recommended (P. C. McIlhiney, Amer. Chem. J. 1894, 16, 408) for the estimation of carboxyl groups. The substance (1 gram) is dissolved in excess of alcoholic potash, the alcohol being at least 93 p.c. The solution is saturated with carbon dioxide until the excess of alkali is precipitated as carbonate or bicarbonate. The precipitate is collected and washed with alcohol, the filtrate is distilled to remove the solvent, and the residue containing the potassium salt of the organic acid is distilled with 10 p.c. aqueous ammonium chloride, the ammonia evolved being estimated in the usual way. Each molecular proportion of ammonia corresponds with one carboxyl group. This method is applicable to the weaker fatty acids.

Carboxyl can be estimated by a method based on the following reaction :—

$$6R{\cdot}CO_2H+5KI+KIO_3=6R{\cdot}CO_2K+3I_2+3H_2O$$

The weighed substance is digested for 12 hours with an aqueous solution of pure potassium iodide and iodate in a stoppered vessel. The mixture containing the liberated iodine is rinsed unto the generating vessel of a gas volumeter and treated with alkaline hydrogen peroxide, when the oxygen evolved

$$I_2+2KOH+H_2O_2=2KI+2H_2O+O_2$$

is a measure of the carboxyl groups originally present ($6CO_2H \equiv 3O_2$) (Baumann-Kux, Zeitsch. anal. Chem. 1893, 32, 129; Annalen, 1904, 335, 4; *cf.* Gröger, Zeitsch. angew. Chem. 1890, 3, 353, 385). It should be noticed that acidic substances not containing carboxyl groups (*e.g.* picric acid) liberate iodine from the iodide-iodate mixture.

Carbonyl.

The carbonyl group, whether present in aldehydes R·CO·H or ketones R·CO·R′, can be detected by means of the following colour-reaction. An aqueous or alcoholic solution of the substance is treated with a 0·5 to 1 p.c. solution of the hydrochloride of an aromatic meta-diamine (meta-phenylenediamine or its homologues), when in a few minutes an intense green fluorescence is developed, which attains its maximum intensity after two hours. All aldehydes give this reaction, but the mixed ketones and ketonic acids do not (Windisch, Zeitsch. anal. Chem. 1888, 27, 514).

Practically all aldehydes restore the colour to the following solution (Schiff's reagent). A litre of 0·10 p.c. magenta solution is decolourised by adding 20 c.c. of sodium bisulphite solution (30°Bé.) followed after one hour by 10 c.c. of concentrated hydrochloric acid. (For the exceptions, *cf.* Bittó, Zeitsch. anal. Chem. 1897, 36, 375.) The reaction has also been utilised quantitatively (McKay Chase, J. Amer. Chem. Soc. 1906, 28, 1472; Schimmel & Co., Ber. 1907, 123).

Phenylhydrazine condenses with aldehydes and ketones, yielding phenylhydrazones. When the mixture is treated with Fehling's solution (70 grams $CuSO_4,5H_2O$, 350 grams Rochelle salt, and 260 grams KOH, in 2 litres), the excess of phenylhydrazine is decomposed, evolving nitrogen :

$$C_6H_5{\cdot}NH{\cdot}NH_2+O=C_6H_6+H_2O+N_2,$$

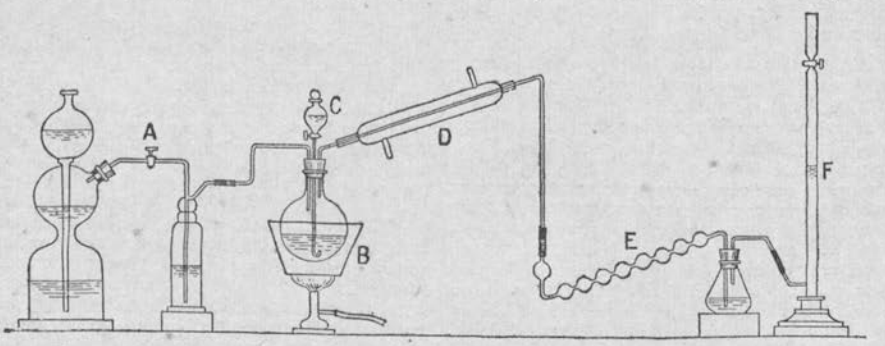


FIG. 33.

while the phenylhydrazone remains unchanged. The estimation is carried out in a flask, B, connected with a carbon dioxide generator, A (Fig. 33). A known volume of Fehling's solution is introduced and covered with a layer of petroleum to prevent the caustic potash from absorbing the carbon

dioxide. A blank experiment is first made with the standard solution of phenylhydrazine hydrochloride and aqueous sodium acetate, the nitrogen evolved on heating the solutions together being collected in a Schiff's nitrometer, F. The experiment is then repeated with the same solutions of phenylhydrazine and sodium acetate *plus* the carbonyl compound; the difference between the two volumes of nitrogen collected is a measure of the carbonyl present in the compound (Strache, Monatsh. 1891, 12, 524; 1892, 13, 299; 1893, 14, 270; Watson Smith, Chem. News, 1906, 93, 83).

When the carbonyl compound (*e.g.* pyruvic acid) condenses readily with phenylhydrazine or its hydrochloride in aqueous solution, the excess of this base can be estimated by adding excess of *N*/10-iodine solution, and titrating the remaining iodine with standard sulphurous acid or thiosulphate, using starch as indicator. This estimation is based on the following reaction:—

$$C_6H_5{\cdot}NH{\cdot}NH_2+2I_2=3HI+C_6H_5I+N_2.$$

The phenylhydrazone is not affected by the iodine solution (E. v. Meyer, J. pr. Chem. 1887, [2] 36, 115; *cf.* Petrenko-Kritschenko, Ber. 1901, 34, 1699; and Annalen, 1905, 341, 15, 150).

Organic amines.

The organic amines are divisible into three classes, primary, secondary, and tertiary, containing their nitrogen atoms combined respectively with one, two, and three organic groups. These groups may be either aliphatic or aromatic, and the reactions of each of the three classes of amines depend very largely on the nature of the organic groups to which the basic nitrogen atom is attached.

Primary amines. The primary amino-group $C{\cdot}NH_2$ may be detected by the carbylamine reaction (Hofmann, Ber. 1870, 3, 767), irrespective of the nature of the organic group, which may be either aliphatic, aromatic, or hydroaromatic (*cf.* Monatsh. 1896, 17, 397). The test consists in warming the substance in alcoholic solution with chloroform and caustic potash, when a carbylamine (iso-nitrile) is produced, which has a pungent disagreeable odour:

$$R{\cdot}HN_2+CHCl_3+3KOH=R{\cdot}NC+3KCl+3H_2O.$$

The primary amines all interact with nitrous acid, but the aliphatic bases are immediately converted into hydroxyl derivatives (alcohols), whereas the aromatic bases furnish diazo-derivatives from which the nitrogen is evolved rapidly on warming or slowly at the ordinary temperature.

In the case of the aliphatic primary amines, this nitrogen can be collected, and the amount indicates the proportion of amino- groups present. As nitrous acid itself decomposes readily, evolving oxides of nitrogen, Stanĕk recommends the use of nitrosyl chloride, obtained by adding fuming hydrochloric acid to 40 p.c. aqueous sodium nitrite (Zeitsch. physiol. Chem. 1905, 46, 263). This reagent can be mixed with saturated salt solution without undergoing decomposition; the aliphatic amino-carboxylic acids (glycine, &c.) can be readily decomposed by it in a current of carbon dioxide, and the nitrogen evolved is freed from the former gas and traces of oxides of nitrogen by passing the mixed gases through alkaline permanganate solution. Half the nitrogen measured in the gas burette corresponds with that originally present in the amino-acid.

In the case of the aromatic primary amines, the acid solution of the base is carefully diazotised at 0° with standard sodium nitrite; the end-point is reached when a drop of the solution gives a blue colour on starch-iodide paper. The sodium nitrite solution may be standardised with either potassium permanganate, sodium sulphanilate ($NH_2{\cdot}C_6H_4{\cdot}SO_3Na,2H_2O$) or para-toluidine (*cf.* Green and Rideal, Chem. News, 1884, 49, 173; Kinnicutt and Nef, Amer. Chem. J. 1886, 5, 388; Zeitsch. anal. Chem. 1886, 25, 223).

Estimation of imino-groups in secondary amines. A weighed quantity of the substance is mixed with a known excess of acetic anhydride, either alone or diluted with dry xylene or dimethylaniline (Bull. Soc. chim. 1892, [3] 7, 142; Chem. Zeit. 1893, 17, 27, 465). After one hour, water is added and the mixture warmed under a reflux apparatus, so that no anhydride is lost by evaporation. The solution is then titrated with standard barium hydroxide and phenolphthalein indicator. The amount of acetic acid present indicates the excess of acetic anhydride left over from the acetylation of the secondary base.

The tertiary amines and the quaternary ammonium salts do not give the reactions of the primary and secondary amines, but the total amount of basic nitrogen present in an organic amine can frequently be ascertained by the analysis of the characteristic salts of the base. The aurichlorides and platinichlorides may frequently be employed for this purpose, as these double salts on ignition leave a residue of the metal, each atomic proportion of gold corresponding to one basic nitrogen atom, while a similar quantity of platinum corresponds with two basic nitrogen atoms. In the majority of cases these double salts have respectively the general formulæ, $RHCl,AuCl_3$ and $(RHCl)_2PtCl_4$, and are obtained in the anhydrous condition; yet, in certain instances, hydrated forms are known and sometimes the salts themselves have an anomalous composition not corresponding with the general formulæ. Evidence obtained in this way should, if possible, be supplemented by the analysis of other salts, and for this purpose the ferrichlorides, chromates, oxalates, thiocyanates, ferrocyanides, picrates, and picrolonates have been employed, as well as the commoner nitrates, sulphates, and halide salts.

Gas analysis.

The experiments of Gay-Lussac established long ago the value, from a scientific point of view, of the determination of the volumetric composition of gases and the products formed by their interaction; but it is only within recent times that the methods of gas analysis have been applied to any great extent for technical purposes. The value of such determinations is now generally recognised on account of the information which they give respecting the efficiency of combustion, the progress of operations in which gases are consumed or produced, and the like.

With few exceptions the volumetric and not the gravimetric composition of the gas is required, and the measurements are essentially measurements of volumes. The gas to be examined is confined over mercury or water in a suitable measuring apparatus, and its composition is determined (1) by treatment with appropriate absorbing reagents and measurement of the contraction produced; (2) by exploding with oxygen or hydrogen and measuring the contraction; (3) by exploding with oxygen or hydrogen, measuring the contraction, and then treating with absorbing reagents, and measuring the second contraction. Sulphur dioxide and some other gases soluble in water are estimated by titration, a definite volume of the gas being drawn through a measured quantity of a standard solution, the excess of which is afterwards determined.

The highly refined and accurate methods of gas analysis employed for purposes of research are of little value for technical purposes on account of the length of time required for their execution. Information respecting these methods may be found in Bunsen's Gasometrische Methoden, 2nd ed. 1887; Sutton's Volumetric Analysis, 9th ed. 1904; Dittmar's Exercises in Quantitative Analysis, 1887; Hempel's Gasanalytische Methoden, 3rd ed. 1900; Travers' Experimental Study of Gases, 1901; *v.* also Thomas (Chem. Soc. Trans. 1879, 35, 213), and Meyer and Seubert (Chem. Soc. Trans. 1884, 45, 581). In this article only those methods will be described which are available for technical purposes.

Measurements.—The volume which a given mass of gas occupies depends on the temperature, the pressure, and the proportion of moisture which it contains. The temperature is ascertained by means of a thermometer attached to or suspended near to the measuring vessel. Measurements are usually made under atmospheric pressure, and this is determined by means of a barometer placed in the room in which the analysis is made. The siphon barometer is a convenient form of instrument for the purpose, and should stand on the table close to the gas apparatus. In case the level of the mercury or water in the measuring tube is higher than that in the trough or the attached tube, the true pressure upon the gas is given by the height of the barometer *minus* the difference between the mercury level inside and outside the tube. If water is used, the height of the water column divided by 13·6 gives the height of the corresponding column of mercury with sufficient accuracy. It is better to eliminate this correction by adjusting the liquid so that it is at the same level both inside and outside the tube, which is easily done.

The gas must be either perfectly dry or saturated with moisture. If an indefinite quantity of water vapour is present, accurate measurements are impossible. It is more convenient to measure the gas when moist, and hence if the gas is confined over mercury a few drops of water are introduced when the tube is filled with the mercury and this water is taken up by the gas. Under these conditions the surrounding pressure is balanced partly by the gas and partly by the aqueous vapour which it contains, and in order to ascertain the pressure which the gas itself is under, the tension of aqueous vapour at the particular temperature must be subtracted from the height of the barometer. The formula for reducing the volume of gas to the standard temperature and pressure (0° and 760 mm.) is:

$$V_0 = \frac{V + 273 \times (B - f)}{(273 + t) \times 760} \text{ or } V_0 = \frac{V \times (B - f)}{(1 + 0{\cdot}00366t \times 760)}$$

in which V is the actual reading; t, the temperature; f, the tension of aqueous vapour at the temperature, t; and B, the height of the barometer. The reduction of the height of the barometer to 0° is necessary for accurate calculation, but may usually be omitted. The following table, abbreviated from Bunsen's Gasometrische Methoden, gives the value of $1+0{\cdot}00366t$ for the ordinary range of temperature:—

$t°$	Number	Log	$t°$	Number	Log	$t°$	Number	Log
0°	1·00000	0·00000	11°	1·04026	0·01714	21°	1·07686	0·03216
1	1·00366	0·00159	12	1·04392	0·01867	22	1·08052	0·03363
2	1·00732	0·00317	13	1·04758	0·02019	23	1·08418	0·03510
3	1·01098	0·00474	14	1·05124	0·02170	24	1·08784	0·03656
4	1·01464	0·00631	15	1·05490	0·02321	25	1·09150	0·03802
5	1·01830	0·00788	16	1·05856	0·02471	26	1·09516	0·03948
6	1·02196	0·00943	17	1·06222	0·02621	27	1·09882	0·04093
7	1·02562	0·01099	18	1·06588	0·02771	28	1·10248	0·04237
8	1·02928	0·01253	19	1·06954	0·02921	29	1·10614	0·04381
9	1·03294	0·01407	20	1·07320	0·03068	30	1·10980	0·04524
10	1·03660	0·01561						

When the estimations are made rapidly, and only approximate results are required, the corrections for temperature and pressure are omitted, since it may be assumed that they remain constant during the analysis.

The following plan, described by Winkler, renders the use of the barometer and thermometer unnecessary, and makes the calculation much simpler. It is an adaptation of William-son and Russell's method of always measuring the volume of the gas at the same degree of elasticity. A tube about 1 metre long, closed at one end and graduated to 120 c.c. in tenths, is moistened internally with a few drops of water, and mercury is poured in in such quantity that when the tube is inverted the mercury stands somewhat higher than 100. The volume which 100 c.c. of air measured at standard temperature

and pressure should occupy under the conditions described, is calculated from the expression:

$$V=\frac{(760-4{\cdot}5)100\times(273+t)}{273(B-f)} \text{ or } \frac{(760-4{\cdot}5)100\times1+0{\cdot}00366t)}{B-f}$$

and air is carefully introduced into the tube until, when the mercury is at the same level inside and outside the tube, it stands exactly at the calculated volume. The tube now contains a quantity of gas saturated with moisture, which, under standard conditions, would occupy 100 c.c., but its actual volume varies in the same ratio as the volume of gas to be measured. The two tubes are allowed to stand side by side, and when the levels have been properly adjusted in each case the volume of the gas to be measured and the volume of the air in the comparison tube are read off. The volume (under standard conditions) of the gas under examination is obtained by the proportion

$$V : V_0 :: V_1' : V_0',$$

in which V is the actual volume of air in the comparison-tube; V_0, its volume under standard conditions, which is always 100; V_1', the observed volume of the gas to be measured; and V_0', its volume under standard conditions.

During the operations the temperature should be kept as constant as possible, and the readings should be taken rapidly, otherwise the proximity of the body will cause variations in the temperature of the gas. It is an advantage to have the measuring tube surrounded by a wider tube which is filled with water. The most accurate method is to take the readings through a carefully levelled telescope (a cathetometer) at a distance of about five or six feet. This also avoids parallax. The measuring tube must be kept vertical, and when water is the confining liquid, sufficient time must be given for the liquid to run down the sides of the tube. Not unfrequently this requires several minutes.

Reagents.

All liquid reagents should be saturated with the gases which they do not absorb chemically. It is desirable that the tensions of these gases in the liquids should be approximately equal to their tensions in the gases which are to be analysed, in order to avoid exchanges between the gas and the absorbing liquid. This is best secured by going through the process two or three times without making measurements, whenever the pipettes have been freshly filled. Liquids used for the analysis of, say, flue gases, should not be used for gases of a different character, *i.e.* which contain the constituents in very different proportions.

Bromine water is used for absorbing olefines. It should be well saturated with bromine and kept in the dark.

Cuprous chloride is made by dissolving 50 grams of cupric oxide in hydrochloric acid, adding 50 grams of copper, and boiling for some time with as little exposure to air as possible. The solution is then diluted to 1000 c.c. with hydrochloric acid of sp.gr. 1·12, and allowed to remain in contact with metallic copper in a closed vessel until the solution becomes colourless. This solution attacks mercury rapidly.

Cuproso-ammonium chloride, obtained by dissolving cuprous chloride in ammonia, does not attack mercury.

The stock solution is made by dissolving 200 grams of cuprous chloride and 250 grams of ammonium chloride in 750 c.c. of water; it is kept in stoppered bottles, and, when required, mixed with one-third its volume of ammonia solution (sp.gr. 0·91).

Hydrogen is obtained by the action of dilute sulphuric acid on pure zinc. The granulated zinc may be placed in a small bottle fitted with a capillary delivery tube, which can be closed by a tap or pinch-cock. The bottle has a tubulus at the bottom, and is connected by a caoutchouc tube with a similar bottle containing dilute sulphuric acid. The latter bottle is raised so that the acid runs on the zinc, and the action is allowed to proceed until the air is completely expelled from the first bottle. The tap is then closed, and the acid is driven back into the second bottle by the pressure of the hydrogen. It is advisable to keep the second bottle at a slightly higher level than the first, to avoid any chance of air leaking in. One of Hempel's tubulated absorption bulbs answers admirably (Fig. 41). The zinc is attached to a cork, which is inserted in the tubulus of the first bulb, and the acid is introduced. When all air is expelled, the capillary tube is closed, and the acid is driven up into the second bulb, so that the pipette is always charged with hydrogen under pressure.

Oxygen is obtained in a pure state by heating potassium chloride *without* manganese dioxide. The powdered chlorate is contained in a glass bulb, the neck of which is drawn out to form a narrow delivery tube.

Phosphorus is employed in the form of narrow sticks, which are made by melting it under warm water and drawing it up into narrow glass tubes. The upper ends of the tubes are closed by the finger, and they are plunged into cold water, when the phosphorus solidifies. It may also be used in a granular form, obtained by shaking the phosphorus vigorously with warm water in a well-closed flask until it solidifies.

Caustic potash (or soda) for Orsat's apparatus is dissolved in three parts of water, and the solution kept in well-stoppered bottles. Hempel uses a solution of caustic potash in two parts of water, which will absorb forty times its volume of carbon dioxide. It may, however, be used somewhat more dilute, and is then less liable to attack the glass.

Pyrogallol is kept in the solid state, and only dissolved immediately before being used. Orsat recommends a solution of 25 grams of pyrogallol in a small quantity of hot water, mixed with 150 c.c. of a solution of 1 part of caustic soda in 3 parts of water. Hempel uses a mixture of 25 c.c. of a 20 p.c. solution of pyrogallol with 75 c.c. of 33·3 p.c. caustic potash solution. This quantity will absorb 200 c.c. of oxygen.

Sulphuric acid of sp.gr. 1·84 is used as a drying agent and for the absorption of nitrogen oxides. Acid of the same strength mixed with so much sulphuric anhydride that it remains liquid at the ordinary temperature but solidifies if cooled, is used for absorbing ethylene and other hydrocarbons.

Water, which is very largely used for confining the gases, should be well saturated with air, but should not contain carbon dioxide. Distilled water is preferable, but any potable water of good quality may be used.

Standard solutions used in the estimation of gases by titration are known as *normal gas solutions* when they are of such strength that 1 c.c. of the solution is equivalent to 1 c.c. of the gas under standard conditions. A normal gas solution of iodine for the estimation of sulphur dioxide would contain 11·333 grams of iodine per litre, and the thiosulphate solution used in conjunction with it would be of equivalent strength.

In many cases it is the weight of the absorbed constituent per cubic metre or cubic foot of gas that is required, and the ordinary standard solutions may be used.

Methods of estimation.

Ammonia, by titration.

Benzene, by absorption in fuming nitric acid boiling at 86°, the nitrogen oxides being then removed by caustic potash. Fuming nitric acid also absorbs carbon dioxide and carbon monoxide. Like the olefines, benzene is absorbed by fuming sulphuric acid and by bromine water, and in fact no absorption method is at present known by means of which benzene and the olefines can be separated (Ber. 1888, 21, 3131).

Carbon dioxide, by absorption in potassium or sodium hydroxide.

Carbon monoxide, by absorption in a saturated solution of cuprous chloride in hydrochloric acid or ammonia. It seems (Ber. 1887, 20, 2754) that these solutions are liable to give off part of the dissolved carbon monoxide, especially after they have been used repeatedly. The error is less with the ammoniacal solution, and is reduced if the solution remains in contact with the gas for some time. The cuprous chloride solution should always be tolerably fresh, and should be saturated with hydrogen, nitrogen, and the other gases which usually occur with carbonic oxide (Ber. 1888, 21, 898). If the amount of carbon monoxide is small, it should be converted by combustion (*v. Hydrogen*) into carbon dioxide, which is afterwards absorbed by caustic potash. If the amount of carbon monoxide is large, the greater part may be absorbed by cuprous chloride, and the remainder removed by combustion and absorption.

The estimation of small quantities of carbon monoxide in air or other comparatively inert gases can be effected by passing the dried gas over solid iodine pentoxide. At temperatures varying from 40°–150° the following reaction occurs: $I_2O_5+5CO=5CO_2+I_2$. Either of the volatile products can be estimated: the iodine volumetrically by standard thiosulphate, or gravimetrically by absorption in a weighed tube containing copper powder; the carbon dioxide may be absorbed in standard barium hydroxide, and the excess of the latter titrated with oxalic acid. If carbon dioxide is present in the gas under examination, it is first removed by potassium or barium hydroxide. Below 60° no hydrocarbon except acetylene reduces iodic anhydride. At higher temperatures several unsaturated hydrocarbons have an appreciable action. Ethylene hinders the oxidation of carbon monoxide by the iodine pentoxide. The process is applicable to air containing one part of carbon monoxide in 30,000, and is used for estimating the monoxide occluded in steel (Gautier, Compt. rend. 1898, 126, 871, 1299; Jean, *ibid.* 1902, 135, 746; J. Amer. Chem. Soc. 1900, 22, 14; 1907, 29, 1589; Ann. Chim. anal. 1910, 15, 1).

Hydrogen is converted into water by combustion with air or oxygen, and the volume of the hydrogen is represented by two-thirds of the contraction consequent upon combustion. If the gas is confined over mercury, an excess of pure oxygen is introduced, the volume read off, and the pressure on the gas reduced considerably below atmospheric pressure by lowering the mercury in the level tube. The lower end of the explosion tube is closed, and combination is initiated by passing a spark from a coil between the platinum wires which are fused into the tube. The pressure is restored to the normal, and when the gas has cooled the volume is again read off.

When the gas is confined over water it is almost impossible to obtain satisfactory combustion, and it is much more convenient to pass the combustible mixture over gently heated spongy palladium. This is prepared by dissolving about two grams of palladium chloride in a small quantity of water, adding a small quantity of a saturated solution of sodium formate and sodium carbonate until the reaction is alkaline. About 1 gram of long and very soft asbestos fibres is introduced, and the pasty mass is dried at a gentle heat. In this way the asbestos is obtained covered with very finely divided palladium. After being completely dried at 100°, it is carefully washed with water to remove soluble salts and again dried. Some of the fibres are moistened and twisted into a thread about 1 cm. long, which is then introduced into the middle of a stout capillary tube, E, about 15 cm. long and 1 mm. internal diameter,

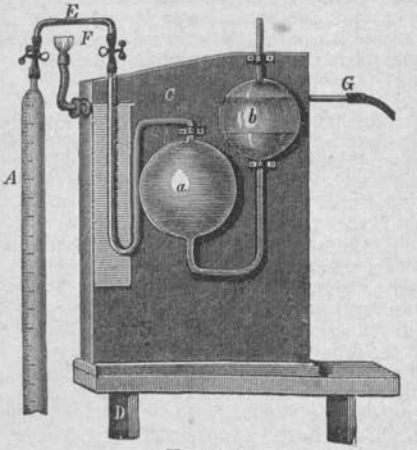


FIG. 34.

and this tube is bent at a right angle at each end. or in any other way convenient for its attachment to the measuring apparatus containing the gas. One end of the capillary is in communication with the graduated tube, A, and the other with a bulb pipette, C, filled completely with water, into which the gas is passed. A small gas or spirit-lamp flame is arranged to heat that part of the capillary which contains the asbestos. When the other gases have been estimated, the mixture of hydrogen and nitrogen which remain

is mixed with air by lowering the level-vessel until the pressure is sufficiently reduced, and then putting the measuring tube in communication with the air. The stop-cock is then closed, the asbestos very gently heated, and the gas passed slowly through the capillary into the bulb and back again three or four times. When combustion is complete, the volume of the residual gas is measured.

This method may be employed in estimating hydrogen in the presence of methane, since the latter is not burnt under these conditions, providing that the temperature does not exceed 500° (J. Soc. Chem. Ind. 1903, 22, 925; 1905, 24, 1202; Zeitsch. angew. Chem. 1903, 16, 695).

The palladinised asbestos can be used in promoting the combustion of carbon monoxide.

Drehschmidt (Ber. 1888, 21, 3245) prefers a platinum tube 20 cm. long and 2 mm. thick, with a bore 0·7 mm. diameter. The bore is almost closed by the insertion of a palladium wire extending through the whole length of the tube. The tube is attached to a burette and an absorption pipette in the same manner as the glass tube; 5 to 6 cm. are heated to redness by means of a gas flame, and the gas is passed backwards and forwards until there is no further alteration of volume. No explosions occur even with mixtures of hydrogen and oxygen containing only a slight excess of the latter.

Hempel has applied the well-known absorption of hydrogen by palladium to the estimation of this gas. Pure palladium is indifferent towards hydrogen in the presence of methane and nitrogen, but when it contains a little palladious oxide combustion of some of the hydrogen occurs, and the heat generated ensures the absorption of the remainder. Palladium sponge is heated and allowed to cool slowly so that it becomes superficially oxidised. A U-tube of 4 mm. internal diameter and 20 cm. total length is charged with 4 grams of this oxidised sponge and maintained at 90°–100° by immersion in a beaker of hot water; this tube is interposed between the gas burette and a pipette filled with water. The absorption is effected by siphoning the gas backwards and forwards through the palladium sponge.

Hydrogen chloride, by titration.

Hydrogen sulphide, by titration.

Hydrocarbons other than olefines are estimated by combustion, preferably with oxygen over mercury under reduced pressure. Acetylene and benzene may be burnt over palladium, but require a somewhat high temperature. Methane cannot be burnt in this way even in presence of hydrogen. The combustion of this gas is effected by mixing it with a considerable quantity of air and aspirating the mixture through a short tube containing cupric oxide heated to redness in a small combustion furnace, the carbon dioxide which is produced being absorbed in standard baryta solution, which is afterwards titrated with standard oxalic acid.

Drehschmidt finds (Ber. 1888, 21, 3249) that a mixture of methane and oxygen can readily be burnt in a platinum tube, as above, if the latter is heated to bright redness. The contraction is observed, and the carbon dioxide formed is removed and the volume again measured.

Nitric oxide is converted into peroxide by admixture with oxygen, and the peroxide is absorbed by caustic potash, the excess of oxygen being afterwards absorbed by alkaline pyrogallate. Nitric oxide may also be absorbed by a concentrated solution of ferrous sulphate, but this method does not give such satisfactory results.

Nitrogen peroxide and nitrous anhydride, by titration; by absorption with sulphuric acid of sp.gr. 1·84; or, in absence of carbon dioxide and other absorbable gases, by absorption with caustic potash.

Olefines, by absorption with fuming sulphuric acid, acid vapours being removed by caustic potash; or by absorption in bromine water, bromine vapours being afterwards removed by caustic potash.

Oxygen, by absorption with alkaline pyrogallate. If the oxygen is present in greater proportion than 20 p.c. a small quantity of carbon monoxide is evolved from the pyrogallol during absorption, and hence the results are slightly too low. After treatment with pyrogallol the gas may be passed into the cuprous chloride bulbs in order to remove any carbon monoxide that may have been formed. Usually, however, this error has no material influence on the results. Oxygen may also be absorbed by phosphorus, and this has the advantage that the presence of carbon dioxide is without influence on the result. The temperature, however, must not be below 18°, and the absorption is prevented by the presence of ammonia, olefines, and other hydrocarbons, alcohol, &c.

Sodium hydrosulphite has been recommended as an absorbent for oxygen, the reaction

$$Na_2S_2O_4+H_2O+O=2NaHSO_3$$

taking place readily at low or high temperatures. The solution contains 50 grams of the salt and 40 c.c. of sodium hydroxide (5 : 7) in 250 c.c. of water, and is used in a pipette filled with rolls of iron-wire gauze (Ber. 1906, 39, 2069).

Oxygen may also be estimated by combustion with hydrogen, either explosively by the spark or over palladium-asbestos. The hydrogen should be evolved from commercial 'pure' zinc and pure dilute sulphuric acid, or in special cases from magnesium and sulphuric acid. One-third of the contraction consequent upon combustion gives the volume of the oxygen.

Sulphur dioxide, by titration.

In the ordinary gases from flues, generators, &c., the constituents are estimated in the following order: Carbon dioxide, olefines and benzene, oxygen, carbon monoxide, hydrogen, methane, nitrogen (as residue or by difference).

If acid vapours are present together with one or more of the above gases, the order of absorption, &c., must be determined by circumstances.

Apparatus and manipulation.

Collecting samples.—The gas to be analysed is usually drawn from the flue, chamber, &c., by aspirating it through glass tubes, which may be termed conducting tubes. When the temperature is high, porcelain tubes may be used; or if the gas has no acid properties, iron tubes can be employed. When samples are constantly taken from the same flue, &c., it is convenient to have a short piece of porcelain or iron pipe cemented into the wall and closed at the outer end with a

plug, which is readily removed when the sample is taken. In cases where the gases are originally at a high temperature and possibly in a state of partial dissociation, it is important to draw the sample slowly through a somewhat long tube in order that the gas may cool slowly, since rapid cooling of the gases may leave them in a partially dissociated condition and thus lead to erroneous results.

The sample may be conveniently collected in the measuring apparatus itself; but where this is not possible, a cylindrical glass tube A, drawn out at the upper end and connected with a stop-cock and capillary tube, and drawn out at the lower end and connected by caoutchouc tubing with a similar tube B, open at the top, makes a convenient sampler. The collecting tube may with advantage be provided with a stop-cock at the bottom. The vessel A is completely filled with water or mercury by raising B to a higher level, and the upper stop-cock is closed. The capillary tube is connected with the conducting tube, and the vessel B is lowered so that when the stop-cock is slowly opened the gas is drawn into A, and the water or mercury collects in B. When A is filled the stop-cocks are closed. The gas is readily transferred from A to the measuring vessel by raising B and carefully opening the stop-cock.

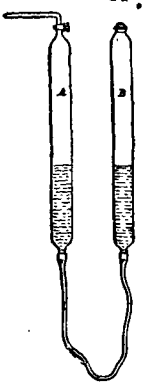


FIG. 35.

In all cases the air in the conducting tube must be expelled, and this is done by placing a T-tube between the end of the tube and the collecting vessel. This T-piece is connected with an aspirator, and the tube is filled with the gas before the stop-cock of the collecting vessel is opened. When the collecting vessel is provided with a three-way cock, the aspirator may be connected directly with the latter. Various forms of aspirator may be used. When the volume of gas to be aspirated is small (*e.g.* in removing air from the conducting tube), a small globular indiarubber aspirating pump is very convenient. For larger quantities of gas, glass

FIG. 36.

FIG. 37.

bottles with a tubulus or stop-cock at the bottom and a tube or stop-cock at the top, or similar vessels of sheet zinc, may be used (Figs. 36 and 37). They are filled with water, the upper tube being connected with the tube which passes into the flue, and the water is allowed to flow from the tap at the bottom. The volume of gas aspirated is determined by measuring the volume of water which flows from the aspirator, and correcting this volume for temperature, &c., in the usual way (*v.* ASPIRATOR).

When aspiration is to be continued for a long time, one of the various forms of water pump may be used. The volume of air aspirated in a given time with a given pressure of water may be determined once for all by direct measurement, or a small gas meter may be placed between the pump and the vessel into which the gas is passed.

If the gas has to be kept for some time before analysis, or if it has to be transported from one place to another, it may be collected in glass tubes which have previously been drawn out at each end. As soon as the tubes are full, the ends are closed by stoppers of indiarubber tubing and glass rod, or are hermetically sealed by fusion. If the quantity of gas is large, cylindrical zinc vessels with conical ends closed by indiarubber corks answer very well.

(For other forms of gas-samplers, *v.* J. Soc. Chem. Ind. 1889, 8, 176; 1903, 22, 190.)

Estimations by titration.—A measured quantity of the appropriate standard solution is placed in a flask or a Woulff's bottle fitted with two tubes, one of which dips into the liquid and is connected with the tube placed in the flue, &c., whilst the other ends just below the cork and is connected with an aspirator. After aspiration has been continued for a sufficient length of time, the excess of reagent is determined by titration. The volume of gas aspirated is determined by the volume of water which has run from the aspirator or by means of a gauge attached to the aspirator. This volume of water, however, represents a volume of gas saturated with moisture and at a temperature and pressure which must be determined by means of a thermometer attached to the aspirator and a barometer in close proximity; the volume under standard conditions is calculated in the usual way. In calculating the percentage composition of the gas, it must be borne in mind that the original volume of the gas was the sum of the volumes of the absorbed constituent and the volume which has passed into the aspirator.

If V_1 is the volume of the absorbed gas, and V_2 the volume which has passed into the aspirator, both under standard conditions, then

$$\frac{100 \times V_1}{V_1 + V_2} = \text{per cent. of } V_1 \text{ by volume.}$$

This method may be applied in the estimation of—

Ammonia, by absorption in sulphuric acid and titration with alkali.

Carbon dioxide (in small quantities), by absorption in standard baryta solution and titration with oxalic acid.

Chlorine, by absorption in a standard solution of arsenious oxide in sodium carbonate, and subsequent titration with iodine after saturating with carbon dioxide.

When hydrochloric acid and chlorine occur together, the latter is determined separately in one quantity, and a second quantity is absorbed in the solution of arsenious oxide in sodium carbonate free from chlorine, and the total chlorine is determined by titration with silver nitrate, using Volhard's thiocyanate method. In calculating the percentage composition, it is important to remember that 1 vol. of chlorine produces 2 vols. of hydrochloric acid.

Hydrochloric acid, by absorption in sodium carbonate and titration with silver nitrate, or, in absence of carbon dioxide and other acids, by absorption in standard caustic potash or soda, and subsequent titration with an acid.

Hydrogen sulphide, by absorption in standard iodine and titration with thiosulphate; or by absorption in bromine water and gravimetric estimation as barium sulphate.

Nitrogen oxides, by absorption in acidified permanganate solution of definite strength, the gas being passed until the solution is just decolourised. This method gives the amount of nitrogen oxides in terms of their reducing power.

Sulphur dioxide, by absorption in standard iodine solution and titration with thiosulphate, or by absorption in bromine water and gravimetric estimation as barium sulphate. The latter plan may be adopted when the proportion of sulphur dioxide is very small and a large volume of gas must be aspirated.

Measuring and absorption apparatus.—Only those forms which have come into general use and are of wide applicability will be described here. Descriptions of the numerous other modifications will be found in Winkler's Chem. Unters. der Industrie-Gase; Winkler and Lunge's Technical Gas Analysis; and in Zeitsch. anal. Chem.

An extremely convenient device which is applied to almost all the forms of apparatus is the three-way stop-cock. This has the usual

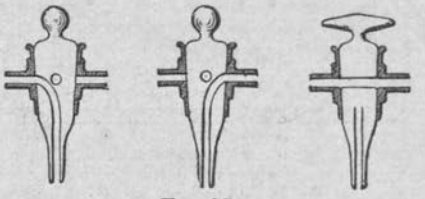


FIG. 38.

transverse bore, but the plug itself is elongated in the form of a tube, the bore of which is continued in a curved direction through the plug and opens at the side in the same plane, but in a direction at right angles to the transverse bore. By means of this tap two tubes can be made to communicate with one another, or either of them separately can be put in communication with a third tube or with the air.

Orsat's apparatus.—The measuring tube or burette consists of a cylindrical bulb terminating at one end in a capillary tube and at the other in a narrow tube of uniform bore graduated in tenths of a cubic centimetre. The total capacity of the tube from the zero to the capillary is 100 c.c., and the lower end of the tube is connected by caoutchouc tubing with a 'level-bottle,' the height of which can readily be adjusted. The burette is enclosed in a cylinder which is filled with water at a constant temperature. The capillary from the upper end of the measuring tube is carried horizontally along a wooden support. Other capillary tubes provided with stop-cocks are fused into it at right angles and communicate by means of very short lengths of stout indiarubber tubing with the absorption pipettes, each of which consists of a pair of somewhat large cylindrical bulbs communicating at the bottom by a curved tube. The bulbs

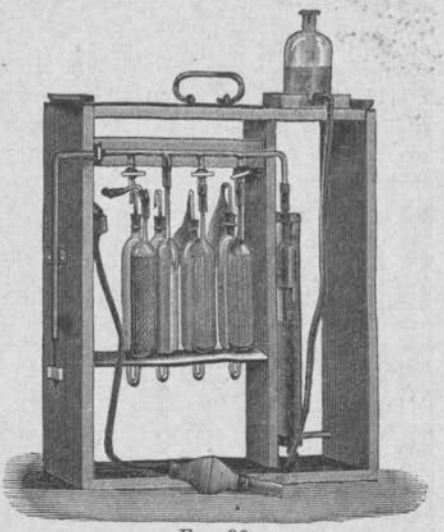


FIG. 39.

nearest the capillary tubes are fitted with short lengths of glass tubing so that a large surface of the reagent may be exposed, and the other bulbs receive the liquids when they are driven out from the first bulbs by the gas. Any number of bulbs can, of course, be attached to the main capillary, and at the end of it there is a three-way tap communicating with the aspirating tube or with the air.

The three absorption pipettes indicated in Fig. 39 are generally filled respectively with solutions of caustic potash, alkaline pyrogallate, and cuprous chloride, and serve for the estimation of carbon dioxide, oxygen, and carbon monoxide.

The burette is filled with water by placing the liquid in the level-bottle and raising the latter, and the stopcocks are then closed. The absorption bulbs are rather more than half filled with the liquid reagents, and by opening the stop-cocks and placing the level-bottle below the apparatus the liquids are drawn up so as to fill completely the bulbs connected with the capillaries. The stop-cocks are then closed.

The burette is filled with water up to the capillary tube by raising the level-bottle, and the far end of the capillary tube is connected with the tube along which the gas is to be conducted. The lower end of the three-way tap is connected with an indiarubber aspirator, and the air is removed from the conducting tube by aspirating the gas through it. The level-bottle is then lowered, the tap is turned through 90°, and the gas is drawn into the burette. When a sufficient volume has entered, the tap is closed, the levels inside and outside the burette are adjusted by raising the level-bottle, and the volume of the gas is read off as soon as the temperature is constant. If it is desired to operate upon exactly 100 c.c., the gas is drawn in until the water is a little below the zero, the tap is closed and the level-bottle is raised so that the gas is slightly compressed and the water rises

above the zero (time having been given for the liquid to run down from the sides of the burette), and the indiarubber tube is closed by a pinch-cock. The level-bottle is again lowered, and by cautiously opening the pinch-cock the water is allowed to descend exactly to the zero, and the pinch-cock is closed. The tap at the end of the main capillary is opened for an instant, so that the excess of gas may escape and the 100 c.c. remaining in the burette may be at atmospheric pressure.

In order to bring the gas into any one of the absorption bulbs, the level-bottle is raised and the tap of the particular bulb is opened. The gas passes into the bulb, and by alternately raising and lowering the level-bottle the gas can be passed backwards and forwards several times, care being taken that the absorbing liquid does not pass through the stop-cock. The gas is finally drawn off so that the absorbing liquid just reaches the stop-cock, the latter is closed, and, after readjusting the levels, the volume of gas is again read off. After making the necessary corrections, the decrease in volume is, of course, the volume of the gas which has been absorbed. The order in which the absorbing liquids should be applied has already been given (p. 236).

Lunge has added to this apparatus a capillary tube with palladium asbestos, for the estimation of hydrogen, connected with a bulb similar to the absorption bulbs, but containing water only. The apparatus also contains a small spirit-lamp carried by a movable rod for heating the palladium asbestos (Dingl. poly. J. 1882, 245, 512).

Sodeau has introduced a modification of Orsat's apparatus suitable for the analysis of mixtures containing only small proportions of combustible gases (*e.g.* chimney gases). In this modification the cuprous chloride pipette and the palladium combustion tube are replaced by a combustion pipette, the only absorption pipettes present being those containing caustic potash and alkaline pyrogallate. The carbon dioxide is first estimated by means of the former, and the combustible gases burnt by passing an electric current (5 amperes) for a short time through a platinum spiral in the combustion pipette. The contraction is noted, and the carbon dioxide produced is estimated by absorption in the caustic potash. These data give the proportions of carbon monoxide and hydrogen originally present in the gaseous mixture. The residual oxygen may now be estimated by absorption in the alkaline pyrogallate (Chem. News, 1904, 89, 61).

Bone and Wheeler's apparatus is a simple form of gas apparatus capable of giving accurate results with almost all gaseous mixtures ordinarily met with in technical practice. The working liquid is mercury, and the apparatus consists of the following parts: (1) A water-jacketed combination of measuring and pressure tubes, A and B, communicating through the glass tap C with the mercury reservoir D; (2) an absorption vessel, F, standing over mercury in a mahogany trough; (3) an explosion tube, E, fitted with firing wires, and having a separate mercury reservoir, H; (4) a sampling tube, K. The connections between A, E, and F are of capillary bore throughout, with suitable glass taps. Before an analysis the whole of the apparatus, including the connections, is filled with mercury,

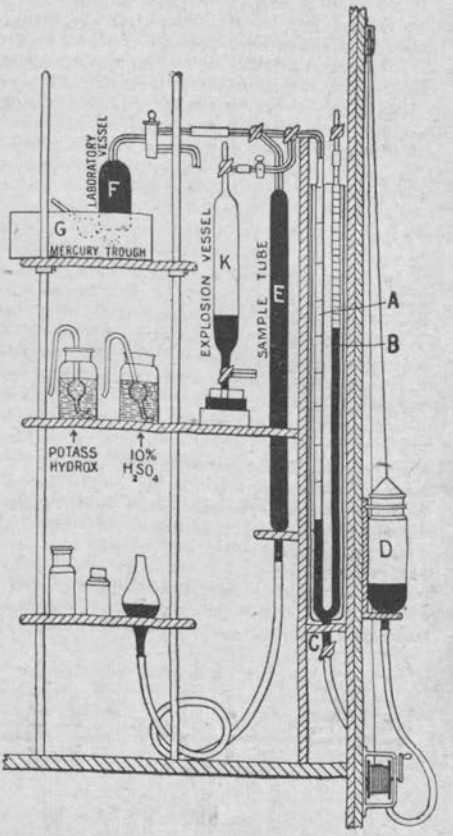


FIG. 40.

and the gas may be introduced either from the sampling tube, K, or from the absorption vessel, F.

The Regnault-Frankland principle of measurement is employed, namely, the measurement of the pressure of the gas (in mm. of mercury) at constant volume. The measuring tube A has a series of constant-volume marks coinciding with the 0. 100, 200, &c., mm. marks on the pressure tube B. These two tubes are moistened with dilute sulphuric acid (1 : 20) as a precaution against the accidental introduction of alkali into the measuring tube. The tap closing the upper end of the pressure tube is connected to it by stout indiarubber pressure tubing; this gives a tight but elastic joint, and obviates risks of fracture. By means of this tap the pressure tube can be rendered vacuous, and, in this way, the measurements are rendered independent of the barometric pressure, and it becomes possible to analyse smaller volumes of gas. The length of the pressure tube provides for the requisite dilution of the explosive mixtures in analyses by explosion. All the absorptions are carried out in the same vessel, F, a comparatively small amount of freshly prepared reagent being used in each operation. The

absorption vessel is rinsed out by means of the three-way tap, the lower parallel limb of which is joined to a large bottle connected up with the water pump. In this way a series of absorptions can be carried out without disturbing a single connection in the apparatus. An analysis of producer gas is easily completed in 45 minutes, and one of coal gas requires about an hour (J. Soc. Chem. Ind. 1908, 27, 10). (For other forms of technical gas apparatus, *v.* F. Fischer, Zeitsch. angew. Chem. 1890, 3, 591; Sodeau, J. Soc. Chem. Ind. 1903, 22, 187. *See* also Chem. Soc. Trans. 1894, 65, 43; 1899, 75, 82; Ber. 1902, 35, 3485, 3493; 1907, 40, 4956; J. Soc. Chem. Ind. 1908, 27, 483, 491; Chem. Zeit. 1903, 845; 1904, 686; Zeitsch. angew. Chem. 1907, 20, 22.)

Hempel's apparatus.—The measuring apparatus consists of a burette, and a plain tube of the same length and diameter, which serves as a level-tube. The burette holds 100 c.c. from the zero to the capillary, is graduated in fifths of a c.c., and terminates at the top in a capillary tube to which is fitted a short piece of stout-walled caoutchouc tubing closed by a pinch-cock. Both the burette and the level-tube are fixed at the bottom into heavy circular stands, and each has a side tubulus near the bottom over which is slipped the caoutchouc tube by which they are connected. It is advisable to make all the joints secure with copper wire. In order to make the measurements more accurate, the burette may be surrounded by a wider tube filled with cold water (Winkler).

The pinch-cock is opened and both tubes are rather more than half filled with water. The burette is completely filled with water by raising the level-tube until the water runs out of the indiarubber tube at the top, and the pinch-cock is then closed. By means of the indiarubber tube the burette is attached to the conducting tube, which has already been filled with the gas, the level-tube is lowered, and the pinch-cock opened. When sufficient gas has been drawn in the pinch-cock is closed, the levels adjusted, and the volume read off in the usual manner. If it is desired to admit exactly 100 c.c., proceed in the same way as described under Orsat's apparatus.

The reagents are contained in absorption pipettes. Simple absorption pipettes consist of

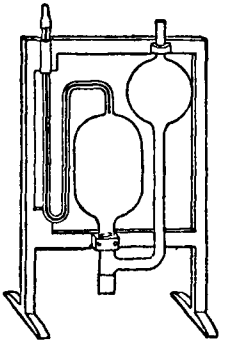


FIG. 41.

two bulbs which communicate at the bottom by a bent tube, one bulb being at a higher level than the other (Fig. 34). The upper part of the lower bulb terminates in a straight capillary tube, which extends to a slightly greater height than the higher bulb, and serves to connect the pipette with the burette. In the tubulated pipette the bottom of the lower bulb is provided with a tubulus, which can be closed with a caoutchouc stopper, and through which solid reagents such

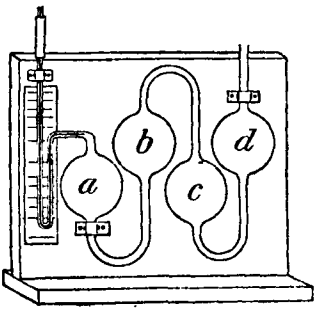


FIG. 42.

as phosphorus or zinc can be introduced. A composite absorption pipette consists of two similar pairs of bulbs, the second pair containing water or some other liquid which protects the reagent in the first from the action of the air. Composite pipettes are used with alkaline pyrogallate, cuprous chloride solution, bromine water, and similar reagents (Fig. 42).

In making the absorptions the pipettes, which are attached to wooden stands, are placed on a table stand of such height that the top of the capillary of the pipette is level with the top of the capillary of the burette. The burette and pipette are joined by means of short pieces of caoutchouc tubing and a short piece of capillary tube bent twice at right angles. The volume of air contained in this capillary is so small that it does not introduce any appreciable error. Care is taken that the capillary of the absorption pipette is filled just up to the top with the reagent. The connections being made, the level-tube, which should be full of water, is placed on the table stand and the pinch-cock is opened. The gas passes into the pipette, and by raising and lowering the level-tube the whole of the gas can be passed backwards and forwards two or three times; or the gas may be allowed to remain in contact with the liquid in the pipette. When absorption is complete, the level-tube is lowered until the reagent is drawn just up to the top of the capillary of the pipette, the pinch-cock is closed, and a second reading is taken.

When combustions of hydrogen or carbon monoxide have to be made, the capillary tube containing palladium asbestos is inserted between the burette and a simple absorption pipette containing water only. With gases containing both methane and hydrogen, the combustion is conveniently effected in an explosion pipette of spherical form, in which mercury is used as the working liquid. The two bulbs of the pipette are connected by thick-walled indiarubber tubing, and the explosion bulb can be closed by two stop-cocks.

When gases very soluble in water have to be measured, a burette is used, provided at the top with an ordinary stop-cock and at the bottom

with a three-way stop-cock, the volume between them being exactly 100 c.c. The burette must be perfectly dry before being filled, an end which is most quickly effected by rinsing the burette with water, then with alcohol, and finally with ether, and passing a current of warm

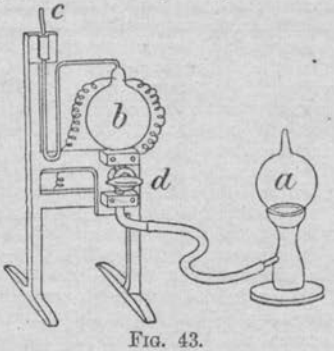


FIG. 43.

air through it. The lower end of the burette is connected with the conducting tube by means of the three-way tap *d*, the other end is connected with an aspirator, and a current of the gas is drawn through the burette until the air is completely expelled. The stop-cocks are then closed, care being taken that the gas in the tube is at

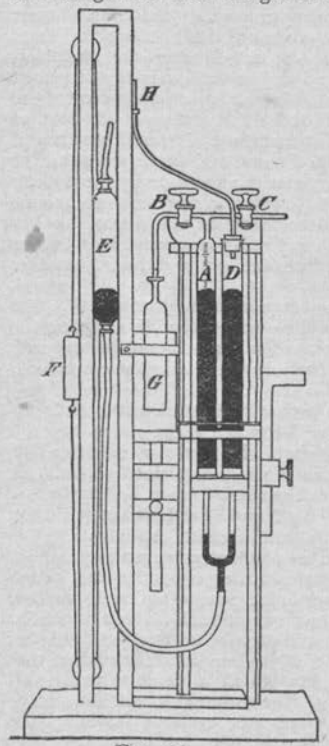


FIG. 44.

FIG. 45.

atmospheric pressure. The absorptions, &c., are made in the same way as with the ordinary burette.

Stead's apparatus consists (Fig. 44) of a graduated tube A, in which all measurements are made, fitted with taps B and C, leading respectively to the absorption vessel and the sampling tube. The lower end of A is joined by means of a T-piece to the mercury reservoir E, and to the tube D, which is open to the atmosphere at H. The readings are taken under atmospheric pressure. The gas sample is collected either directly in the laboratory vessel G or in Stead's sampling apparatus (Fig. 45). From either of these reservoirs a portion of the gas is introduced into the apparatus at C, and thence by opening B into the laboratory vessel G, which contains caustic potash solution standing over mercury. If the gas consists practically of carbon dioxide, carbon monoxide, and hydrogen, it is then

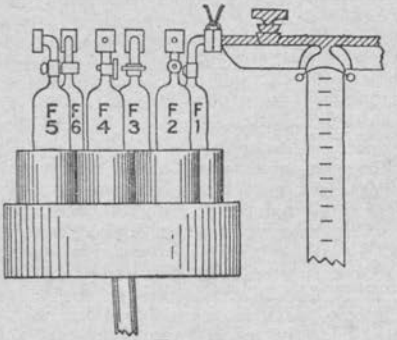


FIG. 46.

mixed with a known volume of oxygen, and the mixture sparked by means of platinum terminals fused into the upper part of the graduated tube A.

The contraction is ascertained and the carbon dioxide produced is estimated, and from these data the amounts of carbon monoxide and hydrogen are determined.

When other absorbable gases are present, then six absorption vessels are employed, and these are carried on a turn-table, so that each in turn can be brought into contact with the measuring tube (Fig. 46). In this modified form of the apparatus the eudiometer tube and each of the absorption vessels are fitted with a perfectly flat piece of plate glass perforated in the centre. These plates are lightly smeared with oil, and when communication is to be made between the eudiometer and the absorption vessel, these face plates are held together by a spring clip (Fig. 47).

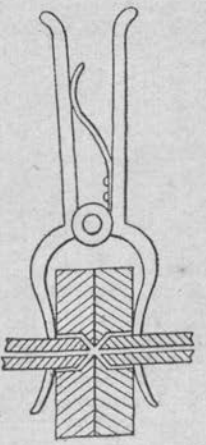


FIG. 47.

A further improvement consists in the use of the modified form of absorption vessel shown

in Fig. 48, in which the reagent is contained in a glass bottle closed by an indiarubber bung

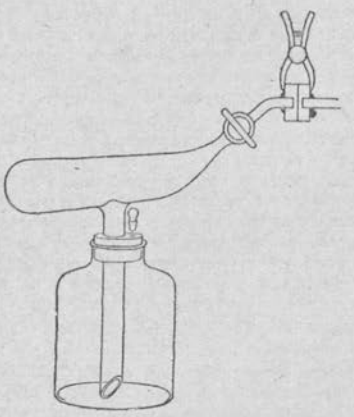


FIG. 48.

carrying a small glass stopper and a pipette furnished with a tap.

By means of these additions Stead's apparatus can be used for the complete analysis of furnace and producer gases and other technically important gaseous mixtures (J. Soc. Chem. Ind. 1889, 8, 178).

The nitrometer, originally devised by Lunge (Ber. 1878, 11, 436) for the estimation of nitrogen oxides in oil of vitriol, is capable of being applied to gas analysis and a large number of other determinations. It consists (Fig. 49) of a burette, fitted at the top with a three-way tap and a cup-shaped funnel, and communicating at

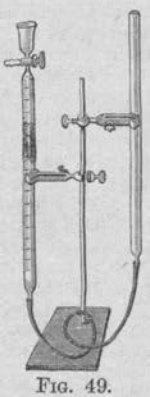


FIG. 49.

FIG. 50.

the bottom by means of caoutchouc tubing with a plain tube of the same diameter, which serves as a level-tube. When large quantities of gas have to be measured, the upper part of the burette is expanded into a bulb, and there is a similar bulb on the level-tube (Fig. 50).

This apparatus is used with mercury, and is thus suitable for the analysis of gases soluble in water. It can be used in the same way as Hempel's burette, and for all purposes to which the latter is applicable. It may also be used without absorption pipettes, the reagent being introduced by means of the cup, but since the reagents cannot be removed without removing the gas, the latter method is only applicable when the reagents do not interfere with each other—*e.g.* for the absorption of carbon dioxide by caustic potash, followed by the absorption of oxygen by alkaline pyrogallate.

The estimation of nitrogen oxides in solution in sulphuric acid is conducted in the following manner. The apparatus is filled with mercury, so that when the tap is open between the burette and the cup, and the level-tube is raised, the mercury just passes through the tap and stands at a height of about 2 inches in the level-tube. The tap is then closed and 2–5 c.c. of the sulphuric acid, according to the quantity of nitrogen oxides which it contains, is placed in the cup, the level-tube is lowered and the tap is turned so that the acid is nearly all drawn into the burette without any air being admitted. To avoid measuring out small quantities (0·5–1 c.c.) of highly nitrated acid, this liquid should be diluted with a known volume of pure concentrated sulphuric acid, and 5 c.c. of this solution taken for analysis. The cup is rinsed with two successive quantities of 2–3 c.c. of pure acid, which is drawn into the cup with the same precaution as before. The tap being closed, the burette is taken out of the clamp and agitated in such a manner that the liquid is brought thoroughly into contact with the first 10 cm. or so of the mercury, which is broken up into bubbles. Nitric oxide is formed and collects in the upper part of the tube. When no more gas is given off, the levels are adjusted and the volume read off after the froth has subsided. In adjusting the levels the difference between the specific gravity of the acid and the mercury is allowed for by taking 6·5 mm. of acid = 1 mm. of mercury. A small quantity of acid is placed in the cup and the tap opened: if the acid is drawn in the pressure in the burette was too low; if gas escapes, the pressure was too high. It is better to err on the side of too low pressure, which is readily corrected by allowing acid to run in from the cup and taking another reading.

In agitating, care should be taken that the drop of acid which collects in the top of the burette just below the tap does not escape contact with the mercury, otherwise the results will be too low.

To prepare for another estimation, the level-tube is raised and the tap is opened so that all the acid and some of the mercury is driven into the cup, and the tap is then turned so that the acid runs out at the side.

The nitrometer may be used for the valuation of nitrites and nitrates, which are introduced in the form of a concentrated aqueous solution, care being taken that the proportion of water to acid does not exceed 2 parts of aqueous solution to 3 parts of the strongest acid. It may also be used for the estimation of nitrates and nitrites in potable waters, and in fact for almost any determinations in which a definite volume of gas is given off. For example, the estimation of carbonic acid; of urea by hypobromite (the reading being increased by 9 p.c. to correct for solubility of the gas and incomplete decomposition); hydrogen peroxide by an acidified solution of potassium permanganate, or, *vice versa*, the value of a permanganate solution by means of hydrogen peroxide, &c. (*See* Lunge,

Ber. 1878, 11, 436; J. Soc. Chem. Ind. 1885, 4, 447, and 1886, 5, 82; Zeitsch. anal. Chem. 25, 309; and the translation of Winkler's Technical Gas Analysis (1885); also Allen, J. Soc. Chem. Ind. 1885, 4, 178.)

The *gas-volumeter*. Several of the estimations referred to in the preceding paragraph are more conveniently carried out in the gas-volumeter devised by Lunge, as in this apparatus

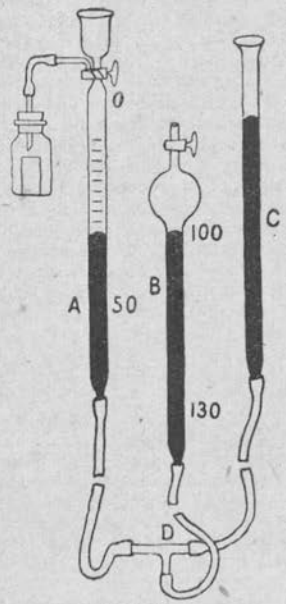


FIG. 51.

the decomposition can be effected in a separate vessel. The measuring tube A and the reservoir C are converted by means of the T-piece D, with the so-called 'reduction' tube B.

At the outset the temperature and pressure are observed, and the volume occupied under these conditions by 100 c.c. of dry (or moist) air measured at 0° and 760 mm. is calculated. The reduction tube is filled with air to this volume, and the tap of the tube closed, or the end of the reduction tube may be terminated by a capillary and sealed off after the volume has been correctly adjusted. A special tap for the reduction tube has been devised by Göckel (Zeitsch. angew. Chem. 1900, 13, 961, 1238). If moist gases are to be measured, a small drop of water is introduced into the reduction tube; if dry gases are under examination, a drop of concentrated sulphuric acid must be introduced into the reduction tube. The formulæ for calculating the volume of gas in the reduction tube are as follows:—

$$V_1 \text{ (dry gases)} = \frac{V_0(273+t)760}{273 \times B}$$

$$V_1 \text{ (moist gases)} = \frac{V_0(273+t)760}{273(B-f)}$$

where V_1 = volume of gas required;
V_0 = normal volume (*e.g.* 100 c.c.);
t = observed temperature;
B = observed barometric pressure;
f = tension of water vapour at observed temperature.

When a decomposition by sodium hypobromite or hydrogen peroxide has been carried out in the auxiliary generating bottle, the gas evolved passes into the measuring tube A. The mercury in A and C are then adjusted to the same level, and the tap *o* closed, the gas being then at the atmosphere pressure. The three tubes are now adjusted so that the mercury in A and B are at the same level when the mercury in the latter tube stands at the 100 c.c. graduation. The gases in A and B are at the same temperature and under the same pressure, and since the gas in B occupies the same volume as it would at 0° and 760 mm. pressure, it follows that the gas in A also occupies the same volume as it would under the standard conditions. In this way, by the use of the gas-volumeter, all thermometric and barometric readings and all reductions by calculations or special tables are avoided; for the volume of gas is read off directly under conditions corresponding to the normal pressure and temperature. It is, however, essential that the reduction tube should be arranged for dry or moist gases according to the nature of the analytical operation involved (*v.* Lunge, Ber. 1890, 23, 440; 1891, 24, 729; 1892, 25, 3157; Zeitsch. angew. Chem. 1890, 3, 129; 1891, 4, 197, 410; 1892, 5, 677; J. Soc. Chem. Ind. 1890, 9, 547. *Cf.* Gruskiewicz, Zeitsch. anal. Chem. 1904, 43, 85).

In addition to the hypobromite and hydrogen peroxide decompositions, Lunge and Marchlewski have adapted the gas-volumeter to the estimation of carbon dioxide in natural carbonates, Portland cement, and other mineral substances, and also to the determination of carbon in iron and steel (Zeitsch. angew. Chem. 1891, 4, 229; 1893, 6, 395; J. Soc. Chem. Ind. 1891, 10, 658). G. T. M.

ELECTROCHEMICAL ANALYSIS.

The first suggestion to apply the electric current to the deposition of metals was made by Cruickshank in 1801 (Nicholson's Journal of Nat. Phil. 1801, 4, 254). He noticed that metals were deposited from acid or alkaline solutions of their salts at the negative pole, and that the metal went into solution at the positive pole. He therefore suggested that the electric current might thus be used as an aid to analysis, particularly for depositing lead, copper, and silver.

In 1812 Fischer suggested its use for detecting small quantities of arsenic (Gilbert's Annalen, 42, 92). In 1840 Cozzi (Arch. delle Science med. fis 50, ii. 208) employed the galvanic current (produced by plates of gold and zinc connected together by a wire) to ascertain whether organic fluids, such as milk, contained metallic impurities. Gaultier de Claubry (J. Pharm. Chim. iii. 17, 125) applied it to detect small quantities of arsenic in animal fluids. In 1861, Bloxam (Quart. Journ. Chem. Soc. 13, 12, 338) described an electrolytic method for detecting arsenic and antimony. Becquerel (Ann. Chim. Phys. 1830, 43, 380) found that manganese and lead were readily oxidised, and appeared as oxides on the anode.

All these workers appear to have merely used the electric current as an aid to qualitative analysis. Wolcott Gibbs (Zeitsch. Anal. Chem. 3, 334), in 1864, showed that copper, nickel, zinc, lead, and manganese might be quantitatively determined by means of the electric current. Lucknow (Dingl. Poly. J. 1865, 177, 231, and 178, 42), from 1860, had employed electrolytic methods for the quantitative analysis of copper salts and for commercial copper. From this time forward many workers entered the field, and about 1880 Edgar Smith in America, and Classen in Germany, very much advanced the subject of electro-analysis, and to-day it is one of the most useful helps to the analytical chemist.

Before dealing with the methods of deposition and separation of the metals, it will be well to describe the apparatus used; but only the apparatus most generally employed will be dealt with.

Classen first suggested the employment of a platinum basin as cathode and a platinum disc as anode. A convenient stand for holding the basin, and a method of connecting with the source of current, are shown in Fig. 52. The basin should hold from 150 to 180 c.c. of solution. The inner surface of the basin should be roughened by the sand blast, as this causes better adherence of the deposit, especially in the case of peroxides such as lead and manganese. The base of the stand is of slate or marble, and the brass rod which conveys the — current is hollow; through this brass rod an insulated wire for carrying the + current passes, and is connected at the top of the rod by means of a piece of ebonite.

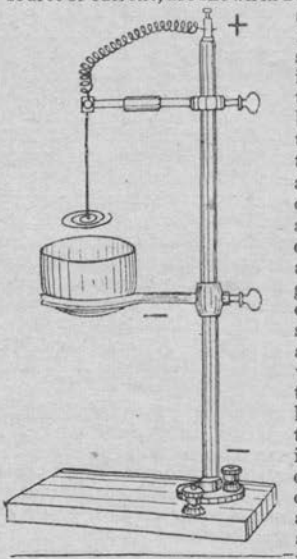


FIG. 52.

The ring which supports the basin has three little platinum points at equal intervals on its circumference; on these the basin rests, thus ensuring good contact. The positive pole of the source of current is connected with the binding-screw fixed to the slate base, and the negative pole with the binding-screw marked —.

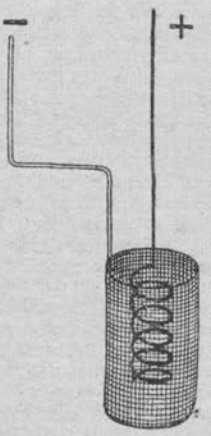


FIG. 53.

Another useful form of electrode is illustrated in Fig. 53. The anode is a stout spiral of platinum and the cathode is a cylinder of platinum gauze. This form of electrode can be employed either for stationary work or for rapid deposition work when the anode is rotated. The vessel in which the electrolysis takes place may either be a beaker, or, better, a funnel with a tap such as is illustrated in Fig. 67.

For stationary work the Flag electrode of F. Mollwo Perkin (Fig. 54) gives very satisfactory results. The cathode consists of a small sheet of stout platinum gauze, autogenously fastened on to a rigid platinum-iridium frame, both frame and gauze being roughened by the sand blast. The wire holds the electrode in position during the analysis. The loop near the top of the wire serves to hang the electrode on the balance. The anode is made of platinum wire, and is bent upon itself in such a way that when it is placed in position for electrolysis, as illustrated in Fig. 55, an even density is obtained on all parts of the cathode.

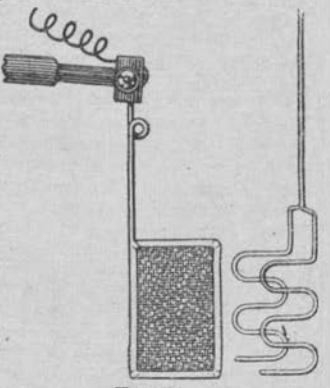


FIG. 54.

It has been found that the rate of deposition of metals from their solutions is very much increased and higher current densities can be employed when either the anode or cathode is rapidly rotated. Frary

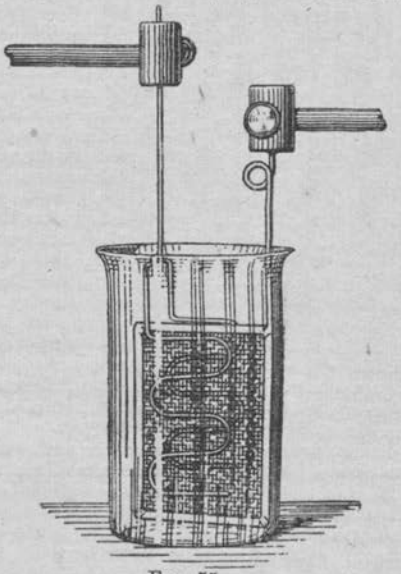


FIG. 55.

(Zeit. f. Elektrochem. 1907, 308) has also shown that excellent results can be obtained by electrolysing with stationary electrodes, but causing agitation of the electrolyte by placing the whole apparatus in the field of a powerful electro-magnet. The forms of the apparatus are depicted in Fig. 56. From the figure it is seen that the solution is contained

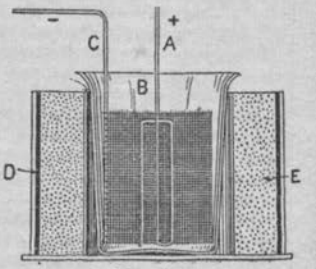


FIG. 56.

in a beaker B, in which is a cylindrical platinum gauze cathode C and a heavy platinum wire as anode A. The beaker is placed in the centre of a spool made from insulated copper wire E. By passing an electric current through the copper wire of the spool, a powerful magnetic field is produced, in the centre of which the beaker stands. If now a current be passed through the electrolyte by means of the electrodes, the electric lines of force are cut at right angles by the magnetic lines of force, and this produces a tendency for the solution to rotate, owing to the vertical magnetic field and radial current lines. The speed of rotation depends upon the ratio between the electric current and the magnetic current. With an electrolysing current of from 6 to 7 amperes, Frary was able to deposit 0·850 gram copper in 15 minutes. The other form, illustrated in Fig. 57, is for electrolysing with a mercury cathode, the use and applications of which will be described later. The electrolysing vessel is ring-shaped, so that it may fit into a hole cut into the pole D of the magnet. An iron rod passes from the other pole up into the centre of the electrolysing vessel. A is the anode and C the cathode. Extremely rapid rotation is thus produced, because the iron core very much facilitates the passage of the magnetic current, there being a radial field with vertical current lines.

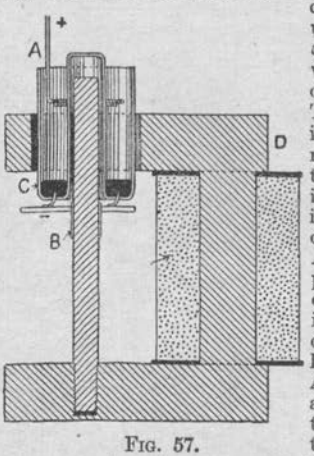


FIG. 57.

The advantages claimed for this method are: rapidity of deposition, and, as there are no mechanical parts which require lubrication, there is no chance of contamination from oil or grease accidentally falling into the solution. As a matter of fact, however, rapid methods of electrolysis are more frequently carried out by means of a rotating anode or cathode.

Gooch and Medway (Amer. J. Sci. 15, 320) use a rotating cathode. It is made from a platinum crucible of about 20 c.c. capacity. The crucible is attached to the shaft of the electromotor, which is used to rotate it at a speed of from 600 to 800 revolutions per minute by fitting it over a rubber stopper with a central bore, into which the end of the shaft fits tightly. In order to make electrical connection between the crucible and the shaft of the motor, a narrow strip of sheet platinum is soldered to the shaft and bent upwards along the sides of the stopper. This connects the shaft with the inside of the crucible when the latter is pressed over the stopper. The anode consists of a half cylinder of sheet platinum. Fig. 58 represents the arrangement of the apparatus when fitted together.

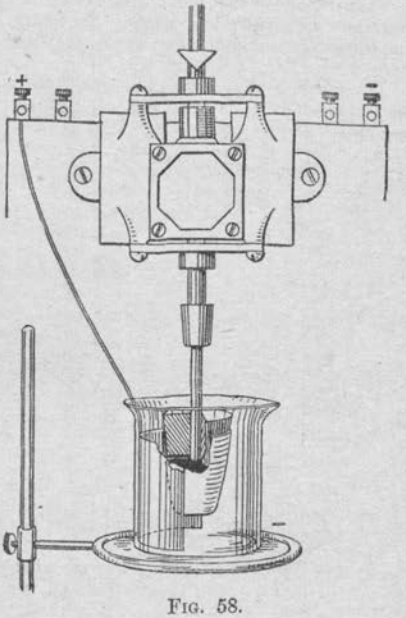


FIG. 58.

F. Mollwo Perkin and W. E. Hughes (Trans. Faraday Soc. 1910, 14) use an electrode of sheet platinum spun up so as to form a narrow thimble (Fig. 59), the upper end being open and having a stout iridio-platinum wire fused on to it by means of three short wire supports. This electrode is fixed into a small chuck and rapidly rotated by means of an electromotor, the speed of rotation usually being from 750 to 950 revolutions per minute. When in use, about two-thirds of the length of the thimble is dipped into the electrolyte, the active surface being about 16·3 sq. cm. If dipped too deeply into the solution, there is a tendency for the liquid to splash into the interior of the cylinder, and this would, of course, lead to erroneous results. The anode consists of a platinum cylinder of fine mesh. It is, however, frequently more satisfactory to employ a rotating anode and a stationary cathode, and for this purpose the gauze anode is employed as cathode, and the anode consists of a spiral of stout iridio-platinum wire. The simplest arrangement is illustrated in Fig. 53. The electrolysing vessel consists of a tap funnel which, when the electrodes are covered, holds about 60 to 70 c.c. of solution. The advantage of this form of electrolysing vessel is the ease with which the electrolyte can be removed on the completion of the electrolysis and the electrodes washed. The method of procedure is to place a beaker beneath the tap and draw off the solution until about half of it has run in. Distilled water is then run up to the original mark and the solution drawn off as before. The operation is repeated until the ammeter needle sinks to zero. The remaining water is

FIG. 59.

run off, the tap closed, and the funnel filled with pure methylated spirit. This is run off, and,

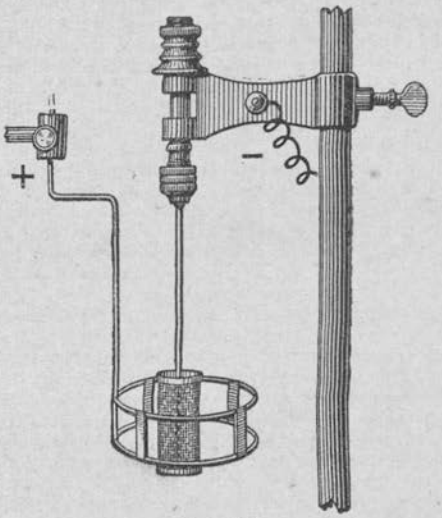


FIG. 60.

after a final washing with absolute alcohol, carried out in the same manner, the electrodes are removed and the cathode dried in the steam oven.

Another form of rotating cathode devised by Perkin is illustrated in Fig. 60. The cathode consists of a cylinder of platinum gauze. The anode is in the form of a double circle of stout platinum wire, and has four small baffle plates so placed as to prevent it from rotating with the cathode.

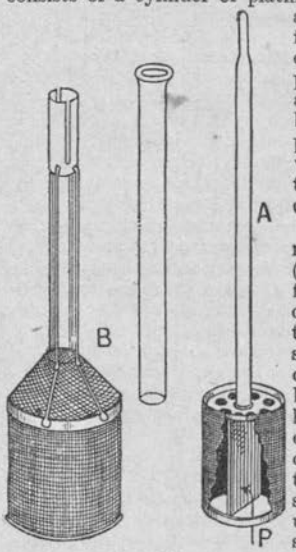


FIG. 61.

In order to rotate the anode (or cathode), it is fixed into a small chuck fastened on to the end of the spindle of a bicycle hub. The barrel of the hub has an arm fastened into it which can be clamped to any suitable support. The upper end of the spindle has a sheaf of pulleys fastened to it, so that it can be rotated by means of a belt from a motor and different speeds be obtained. It is found that the current passes very well through the barrel of the hub and the balls, which are lubricated with oil and graphite, to the spindle, and so to the electrode. When it is desired to obviate all drop in potential, *e.g.* if the apparatus is to be used for graded potentials, then a mercury cup is fastened on to the top of the spindle so that the current passes directly to the spindle.

The apparatus of H. J. Sand (Trans. Chem. Soc. 1907, xvi. i. 373) is rather more complicated, but gives equally satisfactory results.

The special object in the design of this electrode was to produce an apparatus which could be satisfactorily employed for the separation of metals by graded potentials. It consists of a pair of platinum gauze

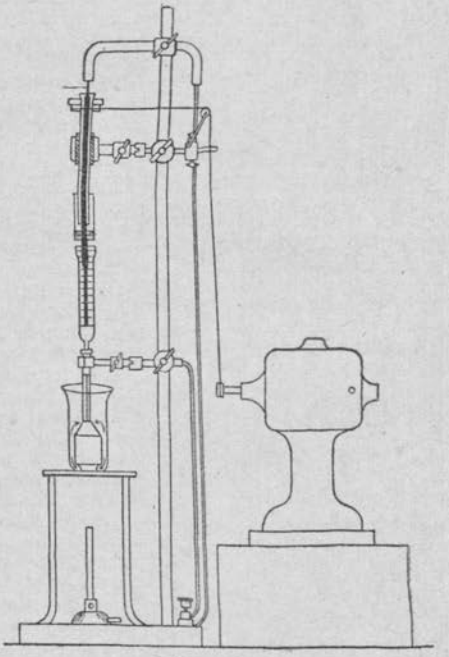


FIG. 62.

electrodes (Fig. 61), an inner rotating electrode A, and an outer electrode B. The two are kept in position relatively to each other by means of a glass tube, which is slipped through the collar and the ring of the outer electrode B. It is gripped firmly by the former, but passes loosely through the latter. The hollow iridio-platinum stem A of the inner electrode is passed through the glass tube, in which it rotates freely. The mesh of the gauze is 14^2 per sq. cm. The gauze of the outer electrode almost completely stops the rotation of the liquid. The electrolyte is, therefore, ejected rapidly from the centre of the inner electrode by centrifugal force, and is continually replaced by liquid drawn in from the top and the bottom. So great is the suction thus produced, that when the electrode is moving rapidly, chips of wood or paper placed in the solution are drawn down to the top of the outer electrode. The circulation is practically independent of the size of the beaker employed. As the outer electrode surrounds the inner completely, the lines of flow of the current are contained between the two, and even when strong currents are employed, the potential

of the electrolyte anywhere outside the outer electrode is practically the same as that of the layer of liquid in immediate contact with it. Fig. 62 shows the apparatus with stand and motor in working order. Before the method adopted for electrolysing by means of graded potential is discussed, the mercury cathode devised by Smith and Howard will be described.

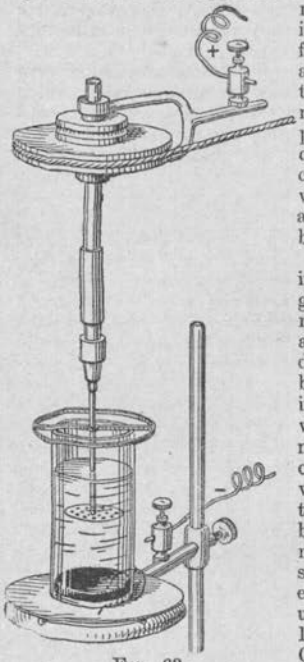


FIG. 63.

WolcottGibbs, in 1880, first suggested the use of metallic mercury as cathode, a definite amount being weighed into a beaker, where it was connected by means of platinum wire with the negative pole of a battery. Various metallic salt solutions were experimented upon, and, in 1883 (Amer. Chem. J. 13, 571), Gibbs stated that 'It was found possible to separate iron, cobalt, nickel, zinc, cadmium, and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the respective liquids.' Gibbs had in view not only the determination of the metals, but also of the anion left in the solution by titration.

In 1886 Luckow (Chem. Zeit. 9, 338, and Zeitsch. anal. Chem. 25, 113) suggested the addition of a known weight of a solution of a mercury salt to a solution of zinc sulphate, and so to deposit zinc and mercury simultaneously. In 1891 Vortman (Ber. 24, 2749) suggested a similar method, and employed it in the determination of several metals. Drown and McKenna (Amer. Chem. J. 5, 627) further worked at the subject, using an apparatus somewhat similar to Wolcott Gibbs, that is to say, an actual mercury cathode, but the process was first successfully worked out by Edgar Smith and his collaborators (J. Amer. Chem. Soc. 25, 885). The apparatus employed consists of a small tube or beaker of about 50 c.c. capacity, close to the bottom of which a thin platinum wire is introduced by means of which the current is supplied to the mercury cathode (Fig. 63).

The external part of the platinum wire touches a disc of sheet copper on which the beaker rests, and which is connected with the negative source of the current.

The anode is either a perforated disc of platinum or a stout spiral of platinum wire. During the electrolysis the anode is rapidly rotated by means of an electromotor or water turbine.

The chief difficulty in using the mercury cathode is the trouble experienced in washing and drying it. The solution left at the end of the electrolysis is siphoned off, and at the same time distilled water is run in until the needle of the ammeter drops to zero. Then, and not till then, the current is switched off. The inside of the beaker and the amalgam are rinsed with alcohol three times, and finally with dry ether. It is advantageous, in order to drive out thoroughly the last traces of ether, to blow dry air into the beaker for a few minutes. After standing for half an hour, the apparatus is ready for weighing. F. M. Perkin (Trans. Faraday Soc. 1910, 14) uses a small quartz beaker as containing vessel, with an iridium wire fused into it to make contact with the mercury. The advantage of iridium is that it does not amalgamate with the mercury. An advantage of the quartz vessel is that it can be heated to redness for purposes of cleansing. The apparatus is illustrated in Fig. 64. It will be noticed that a siphon tube is fused into one side of the beaker. The layer of mercury must not be sufficient in quantity to close the side tube. A spiral iridio-platinum anode is employed. When the electrolysis is finished, a piece of rubber tube is fastened to the bent end of the siphon. Distilled water is added so that the solution begins to siphon over into a beaker placed below the rubber tube. In order to work with as small a quantity of water as possible and in cases where the solution is required again, *e.g.* in metal separations, the solution is allowed to run out until its level drops almost to the end of the anode. Fresh water is then run in, and the operation repeated until the ammeter needle points to zero. For purposes of steadiness the vessel is held between clips on a copper plate.

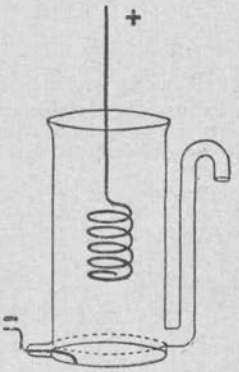


FIG. 64.

By means of the mercury cathode not only can the cations be rapidly and accurately determined, but also the anions remaining in the solution.

Method of Graded Potential.

Each metal has a particular potential at which it begins to be deposited; below this potential it is not possible to deposit the metal. It follows, therefore, that when dealing with a solution containing the salts of two or more metals it will be possible, provided the deposition potentials of the metals do not lie too near together, to deposit separately the metals, by first working with the lowest potential at which one of the metals will be deposited. When this metal has been deposited the next one in the potential series will be deposited if the potential is raised.

This method of analysis was suggested by Kiliani in 1883, and was further elaborated by

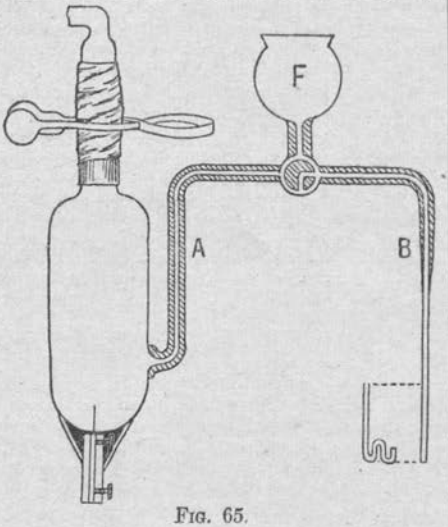


FIG. 65.

Freudenberg working in Ostwald's laboratory (*Zeit. physikal. Chem.* **12**, 97). But it was

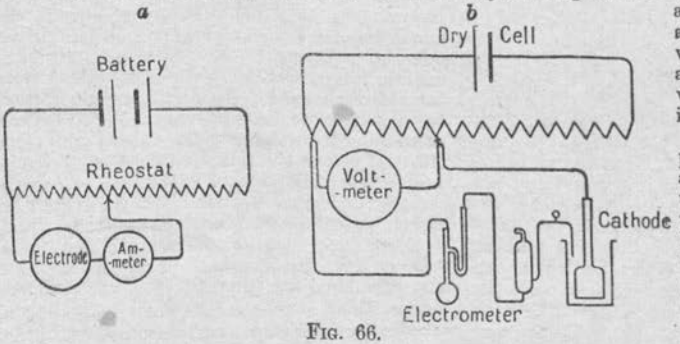


FIG. 66.

H. J. S. Sand (Trans. Chem. Soc. 1907, 373) who first worked out the method and used the apparatus with the rotating cathode already mentioned. The potential is kept at constant value by means of an *auxiliary electrode*. Such an auxiliary electrode, designed by Sand, is illustrated in Fig. 65. It is a mercury-mercurous sulphate $2N$-sulphuric acid electrode. The distinctive feature of the electrode is in the funnel F, and connecting glass tube AB. The two-way tap allows the funnel F to be connected with either limb of the glass tube AB, or closes all parts from each other. The limb A permanently contains the $2N$-sulphuric acid solution of the electrode. But the limb B is filled for each experiment from the funnel F with a suitable connecting liquid, generally sodium sulphate solution. The end of B is made of thin tube of about $1\frac{1}{2}$ mm. bore, and is bent round several times to minimise convection. While the electrode is in use, the tap, which must be kept free from grease, is closed, the film of liquid held round the barrel by capillary attraction, making the electrical connection, but towards the end of a determination, a few drops are run out in order to expel any salt which may have diffused into the tube.

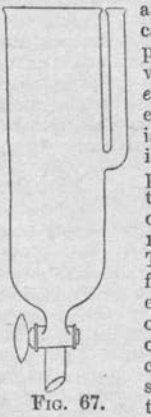


FIG. 67.

Electrical connections.—For separations by graded potential the electrical connections must be made as shown in Fig. 66 *a* and *b*. The battery is connected directly to the two ends of a sliding rheostat, the electrolytic cell to one of them and the slider. It is essential that the sliding contact should be good. The arrangement adopted for the measurement of the potential-difference auxiliary electrode-cathode is one which has been frequently employed in electro-chemical research. The electromotive force to be measured is balanced against a known electromotive force by means of a capillary electrometer. The known electromotive force is drawn from a sliding rheostat, the ends of which are connected with one or two dry cells. The value of the E.M.F. is read directly on a delicate voltmeter (range 1·5 volts). For potential differences greater than 1·5 volts, a Helmholtz 1-volt instrument may be interposed between the auxiliary electrode and the rheostat. The arrangement allows the voltage to be measured almost instantaneously, which is a matter of great importance.

To carry out an experiment, the cathode, anode, and auxiliary electrode are placed in position, the electrolyte is heated to the required temperature, and covered with a set of clock-glasses having suitable openings for the electrodes. For the purpose of a separation, the current is usually started at about 3–4 amperes, and the potential of the auxiliary electrode noted. As a rule, this is only slightly above the equilibrium potential. The current is then regulated so that the potential of the electrode may remain constant. When no side-reactions take place, the current falls to a small residual value (generally about 0·2 ampere), as the metal to be separated disappears from the solution. The auxiliary electrode is then allowed to rise 0·1–0·2 volt, according to the metal.

It is obviously a matter of great importance to know when all the metal has been deposited. Under the conditions just assumed, the amount deposited per unit of time may be taken as roughly proportional to the amount still in solution. This being so, it follows that the amount in solution will decrease in geometrical ratio during successive equal intervals of time. If we, therefore, make the safe assumption that the concentration of the metal has fallen to under 1 p.c. of its original value in the time during which the potential and the current have been brought to their final value, it is clear that by continuing the experiment half as long

again, the concentration of the metal will fall to under 0·1 p.c., so that the deposition can be considered finished.

In cases where side-reactions occur, the current does not fall to zero, but it generally attains a constant value which allows it to be seen when all the metal has been removed. In certain cases this can be tested for chemically, and by continuing the experiment for about half as long again as this reaction demands, the metal may be safely assumed to have been deposited completely. This method may be adopted, for example, in the separation of lead from cadmium, the former being roughly tested for by sulphuric acid. If none of these methods is available, the metal must be deposited to constant weight, or else the separation must be carried out under very carefully defined conditions for a length of time proved by previous experiment to be more than sufficient.

Sand has simplified the apparatus necessary for the potential measurements by fitting all the apparatus required for the measurement of the electrode potential into a single box. Full particulars will be found in Trans. Faraday Soc. 1909, 162.

F. M. Perkin uses the apparatus depicted on p. 248 for working with graded potentials. The vessel containing the electrolyte has a tube fused into the side. Into this side tube the capillary end of the auxiliary electrode is inserted (Fig. 67).

Classification of the Metals for Electro-analytical Purposes.

Most metals can be deposited satisfactorily at the cathode, particularly since the introduction of the mercury cathode and of the graded potential methods. Theoretically, by grading the potential, it should be possible to separate any one metal from another. Indeed, in many cases, this can be done, but there are cases in which the potential differences at which two metals can be deposited, that is to say, the minimum potential at which they will both be deposited, lie so close together that it is not possible to so adjust the conditions that a separation can be effected.

Group I.—Copper, silver, mercury, gold, palladium, rhodium, platinum, iridium, bismuth, antimony, tin, (arsenic), tellurium. These metals are more electronegative than the hydrogen electrode, and, consequently, can theoretically be deposited quantitatively from acid solutions.

Group II.—Cadmium, zinc, and indium. These metals are more electropositive than hydrogen, but, owing to the supertension of the hydrogen evolution in acid solution, it is actually possible to deposit them from weak acid solutions.

Group III.—Iron, nickel, cobalt. These metals are more electropositive than hydrogen, but, as the supertension of hydrogen is very low, these metals cannot be deposited completely from acid solutions. They can, however, be deposited from acid solutions if a mercury cathode is employed.

Group IV.—The metals of this group can either be deposited as oxides at the anode, or as oxides at the cathode. The group comprises the following metals: lead, thallium, manganese, chromium, molybdenum, uranium. Some of them can, however, be satisfactorily deposited as an amalgam on a mercury cathode.

Group V.—The metals of this group are the most strongly electropositive, and can only be deposited by using a cathode of mercury; but even then it is not possible in all cases to obtain a quantitative separation. The metals of this group are aluminium, glucinum, calcium, strontium, barium, magnesium, potassium, sodium, lithium, rubidium, cæsium.

Group VI.—These are all anions, and their estimation has been rendered possible mainly through the work of Edgar Smith, who completely deposits the metals by means of a mercury cathode and estimates the anions by titration or other appropriate method. The most important anions analysed by this method are F', Cl', Br', I', SO_4'', CO_3'', $Fe(CN)_6''''$, $Fe(CN)_3'''$, PO_4''', NO_3'.

It has not been found possible to analyse organic anions by electrolytic methods, because they are either decomposed or various reactions more or less complicated take place. Thus, for example, when the acetate anion is given up at the anode, ethane is produced, which, of course, is given off in the form of a gas.

Nature of Deposit.

Sand (Trans. Chem. Soc. 1907, 383) has theoretically and practically worked out the conditions necessary for obtaining adherent metal deposits.

The production of a *uniform deposit* over the electrode depends entirely upon the relation between polarisation and the E.M.F. required according to Ohm's law to force the current from one part of the solution to the other (Zeitsch. Elektrochem. 1904, 452). The case of metals such as cadmium and zinc, which require a higher potential for their precipitation from most of their solutions than hydrogen, is a question of supertension. The metals can only be deposited by virtue of the supertension which is required to liberate hydrogen as a gas. This supertension varies with the material of the electrode, and may even vary at different parts of the same electrode, owing to different states of its surface. Consequently, it may happen that the metal is deposited on a portion of the electrode which has a high supertension, and will continue to grow there; but at rougher parts of the electrode, where the supertension is lower, hydrogen alone will be evolved. This is, for example, particularly noticeable in the case of zinc, which, instead of being evenly deposited over the surface of an electrode, apparently perfectly smooth and even, often comes out in patches, parts of the electrode being absolutely free from deposit. Some solutions also of the same metal appear to be more sensitive to variations in the quality and character of the electrode than others. Thus with ordinary electrodes when the potential is not graded, it is a matter of the greatest difficulty to obtain an adherent deposit of copper when the electrolyte is sulphuric acid. On the other hand, with electrolytes of potassium cyanide or nitric acid, an even deposit is readily produced.

The nature of the deposit.—Electrolytic deposits may be spongy, coarsely crystalline, or

finely crystalline. The last is the only form in which metals may be deposited in order to yield satisfactory quantitative results. Sand considers (*l.c.*) that spongy deposits are most probably due to the metal being deposited in the form of an unstable hydride, which gradually decomposes with evolution of gas.

The difficulty of hydride formation is got over by keeping the potential of the electrode under control. Vigorous stirring of the electrolyte, small current density, and the presence of some oxidising agent, tend to keep the potential low. But, by using an auxiliary electrode and rapid rotation, it is possible to obtain metals from solutions from which, under ordinary circumstances, they cannot be deposited.

Copper.

Copper may readily be deposited from solutions which contain considerable quantities of nitric or sulphuric acid. But good deposits can also be obtained from cyanide solutions, and it is possible to employ solutions containing an excess of ammonia.

The solutions which give the best results are those containing nitric acid or potassium cyanide. Indeed, it is a matter of considerable difficulty to obtain satisfactory results in presence of free sulphuric acid, excepting when a mercury cathode is employed. For stationary work, either the gauze flag electrode or the cylindrical gauze electrode is to be recommended.

Nitric acid.—About 1 gram of the copper salt is dissolved in about 140 c.c. of water, and 5–10 c.c. of nitric acid (sp.gr. 1·42) added to the solution; that is, from 8 to 10 p.c. of the acid. If the flag electrode is employed, usually about 120 c.c. of water is sufficient, in which case proportionately less nitric acid must be used. The solution may either be electrolysed at ordinary atmospheric temperature, or heated from 45°–50°; in the latter case the time required for the complete deposition of the metal is considerably lessened. The best C.D. to employ is from 0·8 to 1·2 amperes, when the E.M.F. will be from 1 to 2·8 volts. A bright red film will be seen to flash across the cathode almost immediately the circuit is completed. In cold solutions, from 2½ to 3 hours will be required to completely deposit the metal; with hot solutions the rate of deposition is considerably accelerated. To ascertain when the whole of the copper has been deposited, withdraw about 1 c.c. of the solution by means of a pipette, transfer to a test-tube, make alkaline with ammonia, then acid with acetic acid, and add a few drops of potassium ferrocyanide; the formation of a brown precipitate or colouration shows that there is still some copper left in the solution, in which case, of course, it is necessary to continue the electrolysis until, on further testing with the reagent, no colouration is produced.

Washing the deposit.—As the electrolyte contains an excess of free nitric acid in which the copper deposit is readily soluble, the washing has to be carried out with caution. Some workers prefer to siphon off the electrolyte without breaking the circuit, and to run in water at the same time, until the ammeter points to zero. The current is then cut off and the cathode removed, finally washed with distilled water and dipped into a beaker of absolute alcohol. It is then dried in the steam oven, and, after cooling for 20 minutes, weighed. When the gauze cylindrical electrode is used, a stoppered funnel as illustrated in Fig. 67 is very convenient.

The solution is drawn off until only about one quarter of the electrode is immersed. Distilled water is then run in, and the operations repeated until the ammeter shows zero. By operating rapidly, the cathode may be removed, and, if dipped at once into a beaker of water and then washed under the tap or in several changes of water and then in alcohol, absolutely accurate results can be obtained.

The deposit obtained from nitric acid is bright red, and generally has a more or less crystalline appearance. If the C.D. has been too high, it may be 'burnt,' and have a brownish appearance, and may be powdery and non-adherent. When it is desired to electrolyse over-night—and this is often found very convenient—a C.D. of from 0·2 to 0·3 of an ampere is used. It is generally advisable in this case to add more nitric acid, because, owing to the reducing action of the hydrogen liberated at the cathode, the nitric acid becomes converted into ammonia. This formation of ammonia causes the deposit to be spongy and of a bad colour, when it is difficult to wash and weigh. For running over-night about 2 c.c. extra of nitric acid should be added for every 100 c.c. of solution.

The deposits obtained with sulphuric acid are generally not satisfactory, but of all the copper deposits that obtained from solutions containing potassium cyanide is the most beautiful.

Potassium cyanide.—The colour of the deposited metal is pinkish red, and perfectly smooth. But, from other points of view, the deposition from cyanide solutions has no advantage over the deposits obtained from solutions containing nitric acid. The copper salt is dissolved in about 30 or 40 c.c. of distilled water, and then a freshly prepared solution of potassium cyanide added, until the precipitate first produced is dissolved. Slightly more potassium cyanide than is necessary to dissolve the precipitate should be used, but any considerable excess must be avoided. Generally speaking, from 1 to 1·5 grams of potassium cyanide should be used for every gram of copper salt taken.

The C.D. employed should be from 0·8 to 1·2 amperes. The E.M.F. required in cold solutions will be found to be about 5–6 volts; in warm solutions, from 4 to 5 volts. The whole of the copper is deposited in 2 to 2½ hours.

Rapid methods.—By employing rotating electrodes, either rotating anode or cathode, copper may be completely deposited in a few minutes. Thus Sand, by using his apparatus, was able to completely deposit the copper from 0·25 gram copper sulphate in 6 minutes, the number of revolutions of the anode per minute being about 800; in that of Fischer the copper from 0·3 gram copper sulphate was deposited in 10 minutes, the speed of revolution being 1000 to 1200. In the one case a rotating anode was employed and in the other the cathode was rotated. The electrolyte in both cases contained free nitric acid. Cyanide solutions give, however, equally satisfactory results.

Edgar Smith, by employing a rotating anode and mercury cathode, has deposited quantitatively 0·789 gram of copper in 10 minutes, and as much as 0·3945 gram per 4 minutes, the solutions containing sulphuric acid. The advantage of the mercury cathode is that almost any electrolyte can be employed equally satisfactorily. Indeed, the pure salt of the metal may be dissolved in water and electrolysed without the addition of any acid or other electrolyte. When the whole of the metal has been deposited, the solution is run off, and may then be titrated in order to determine the anion, *e.g.* SO_4'' (p. 247).

Silver.

Silver can best be deposited from solutions containing potassium cyanide. From solutions containing other electrolytes it is apt to be deposited in a crystalline feathery form, and consequently does not adhere well to the cathode. There is, however, a tendency for the results to be slightly too low when cyanide solutions are employed. It is very important that only the purest potassium cyanide be used in making up the solutions. For 0·5 gram of a silver salt about 3–4 grams of potassium cyanide will usually be found sufficient. With a C.D. of 0·5 to 1·0 ampere, and a temperature of 50°–60°, the silver will be deposited in from 1 to 2 hours. Using a cold solution and with a C.D. of from 0·2 to 0·35 ampere, the time required is from 4 to 4·5 hours. The deposit should either be washed by siphoning, or the electrode must be very rapidly removed from the electrolyte and dipped into water, in order to avoid loss by the solvent action of the potassium cyanide.

With rotating electrodes the silver can be deposited within a few minutes. By using an auxiliary electrode and rotating the anode vigorously, Sand was able to deposit silver from ammoniacal solutions in 7 to 8 minutes.

Smith, by using a mercury cathode and rapidly rotating anode deposited 0·2240 gram of silver from silver nitrate in 4 minutes. At the commencement of the operation an anodic deposit of silver peroxide was obtained, but after a minute or two this disappeared.

Mercury.

Many methods have been devised for precipitating mercury on platinum cathodes, and some of them give quite satisfactory results. When mercury is deposited on a platinum dish, or on a wire gauze electrode, it spreads evenly over the surface as a thin metallic film, which, however, is inclined to run together as the amount of mercury on the electrode increases in quantity. After the mercury has been deposited, the electrode is washed with water in the usual way, then in absolute alcohol, and finally in absolute ether. The last traces of ether may be removed by blowing dry air on to the electrode.

On no account may the mercury-coated electrode be heated. If the electrode is washed once in 90 p.c. alcohol, and then placed in a beaker of anhydrous acetone for a minute, it may then be dried without using ether. It is always advisable, before weighing, to place the electrode in a desiccator for 20 minutes. The desiccator should have a dish in it containing a little metallic mercury, because even at ordinary temperatures mercury volatilises to a small but appreciable extent.

The mercury can be removed from the electrode by heating in the Bunsen flame, but owing to the tendency for electrolytically deposited mercury to alloy with platinum, the electrode is almost invariably marked with black stains, and a slight loss in weight takes place. For this reason some workers prefer to plate the electrode with copper or silver before using. These difficulties are, however, entirely eliminated by using a mercury cathode; in fact, it is strongly recommended to employ always a mercury cathode when dealing with mercury.

Many electrolytes have been suggested, and all give more or less satisfactory results. Thus, the mercury salt may be dissolved in water and electrolysed in presence of a small quantity of sulphuric, hydrochloric, or nitric acid. With sulphuric acid, from 1 to 2 c.c. of the concentrated acid are added to each 100 c.c. of solution, and electrolysis conducted with a C.D. of 0·3–0·8 ampere per square decimeter, which is finally increased to 1 ampere towards the end of the operation. With rotating electrodes, currents of from 4 to 6 amperes per square decimeter may be employed. The temperature of the electrolyte may be 50°–60°, but not higher. Sometimes, owing to the reducing action of the hydrogen given off at the cathode, mercurous salts are precipitated. The addition of small quantities of ammonium persulphate will cause them to go into solution again. The conditions with the other acids mentioned are very similar to those required for sulphuric acid. Potassium cyanide is not to be recommended, owing to slight solution of the anode taking place.

Sodium sulphide gives very satisfactory results, but care must be taken to employ a very pure solution of salt. From 25 to 30 c.c. of the concentrated solution of sodium sulphide are required for every 100 c.c. of solution. The solution should be heated to about 65°, and for stationary electrodes a C.D. of 0·15–0·25 ampere per square decimeter used. With rotating electrodes from 3 to 6 amperes per square decimeter may be used.

With mercury electrodes rotating anodes are almost invariably used, and high-current densities can be safely employed. The whole of the mercury can be deposited in from 15 to 25 minutes.

Cinnabar may be dissolved in *aqua regia*, the solution evaporated to dryness. The residue is then taken up with water, filtered from gangue, and then directly electrolysed after the addition of a small quantity of nitric acid.

Gold.

Gold may be deposited from its solution in cyanide or in sodium or potassium sulphide, or in ammonium thiocyanate. The drawback to using potassium cyanide is the tendency for the anode to go into solution. But with low-current densities, this only takes place to a small extent. The solution is made up by adding rather more than the quantity necessary of potassium cyanide to bring the gold salt into a clear solution. With stationary electrodes a C.D. of 0·6–0·8 ampere is employed at a temperature of 50°–60°, the metal being deposited in the course of 2 to 3 hours. With rotating electrodes a current of about 3 amperes may be employed, when the metal will be deposited in about 30 minutes.

Sodium sulphide.—From 20 to 25 c.c. of a saturated solution of sodium sulphide are used for every 100 c.c. of solution. With a C.D. of from 0·1 to 0·3 ampere the metal will be deposited in from 4·5 to 5·5 hours. With rotating electrodes and high-current densities, the results are too high, owing to deposition of sulphur along with the gold.

Ammonium thiocyanate.—5 to 7 grams of ammonium thioycanate are dissolved in about 80–90 c.c. of water at 70° to 80°, and the gold solution run slowly in with constant stirring. The clear solution is electrolysed at a temperature of 40°–50° with a C.D. of 0·2–0·55 ampere, the metal being deposited in from 1·5 to 2 hours. This method has not been tried with rotating electrodes. The precipitation of small quantities of yellow canarine in the electrolyte during electrolysis does not interfere with the reaction.

E. F. Smith obtains good results by electrolysing a gold chloride solution, using a mercury cathode. In order to prevent the chlorine evolved attacking the anode, from 10 to 12 c.c. of toluene are added. The time required to deposit 0·15–0·2 gram of gold is about 5 to 7 minutes.

Most solvents for gold will also attack the platinum cathode. *Aqua regia*, for example, cannot be used to dissolve the gold from the platinum. F. M. Perkin recommends a dilute solution of potassium cyanide to which is added 4–5 c.c. of hydrogen peroxide, or from 2 to 3 grams of an alkali persulphate. On gentle warming the deposit is removed in a few seconds.

$$2Au+4KCN+H_2O_2=2KAu(CN)_2+2KOH.$$

Platinum.

Like gold, platinum can be deposited from solutions containing free mineral acids, but unlike gold, which from these solutions is deposited in a non-adherent form, it may be deposited with very feeble currents in a hard and reguline condition. With high currents and with stationary electrodes the metal is always deposited as platinum black. With a current of from 0·01 to 0·05 at a temperature of 50°–60°, about 0·1 gram of platinum can be deposited in 4·5 to 6 hours. Julia Langness (J. Amer. Chem. Soc. 1907, 459), by using a rotating cathode, deposited 0·2 gram of platinum from a solution of K_2PtCl_6 in 5 minutes. But the current, 17 amperes, must be looked upon as excessive for analytical purposes.

Before depositing platinum it is advisable to coat the cathode with silver.

Rhodium.

This metal may be deposited on to a silver-coated electrode from solutions acidified with phosphoric acid. A current of 0·18 ampere is used. As the process continues, the purple colour of the solution gradually disappears and becomes colourless, when the deposition is finished. With a rotating anode the metal may be deposited from solutions weakly acidulated with sulphuric acid in about 15 minutes with a current of 8 amperes, and with a current of 14 amperes in 5 minutes. The deposited metal has a black colour, but is quite adherent.

Palladium.

In order to obtain a dense and firmly adhering deposit of this metal from acid solutions, it is, according to Amberg (Zeit. f. Elektrochem. 1904, 386, 853, and Annalen, 1905, 235), necessary that the potential should not exceed 1·25 volts. With stationary electrodes the process is very slow, and polarisation at the anode takes place, owing to the formation of oxy- compounds. On the other hand, by using a rotating electrode and solutions of palladium ammonium chloride with 30 p.c. by weight of sulphuric acid and a C.D. of from 0·23 to 0·50 ampere, as much as 0·3–0·9 gram may be deposited in from 3·5 to 5 hours.

Julia Langness, by using currents of from 15 to 17 amperes, and an ammoniacal solution, has obtained quantitative deposits in from 3 to 5 minutes.

Antimony.

This metal may be deposited from its thio-salts, particularly sodium thioantimonite, a method originally suggested by Classen. During the electrolysis there is, however, a danger, owing to the deposition of sulphur at the anode, for sodium thioantimoniate to be formed, and this prevents the quantitative deposition of the metal. A. Fischer (Ber. 1903, 2474) recommends the addition of potassium cyanide to the electrolyte, which prevents the formation of the thioantimoniate, thus:

$$N_2S_4+3KCN=3KCNS+Na_2S.$$

There is one difficulty when sodium sulphide is used—the results obtained are usually slightly too high. This is due to the occlusion of small quantities of sulphur along with the metal. For this reason large quantities of metal should not be deposited by this method. The antimony salt is dissolved in 60–80 c.c. water made just alkaline with sodium hydroxide, any precipitate being ignored, then 20–25 c.c. of a fresh saturated solution of sodium sulphide added, and 2·5–3 grams of potassium cyanide. The solution is then electrolysed at from 30°–40°. With stationary electrodes the metal is deposited in from 4·5 to 6 hours; when rotating electrodes are used, in 30 to 45 minutes.

F. M. Perkin and H. D. Law (Trans. Faraday Soc. i. 262) recommend neutral tartrate solutions. The antimony salt is dissolved in water, and from 8 to 10 grams of ammonium tartrate added; if necessary, the solution is neutralised with dilute ammonia. At a temperature of from 70° to 80°, and a C.D. of 0·25–0·55 the metal can be deposited with stationary electrodes in from 2·5 to 3 hours.

Sand (Chem. Soc. Trans. 1908, 1572) dissolves the metal in 20 c.c. of hot conc. sulphuric acid, and dilutes the cold solution to 80 c.c. The solution becomes turbid owing to hydrolysis, but this disappears during the electrolysis, and does not affect the result. The auxiliary electrode potential is kept at from 0·55 to 0·65, but may be increased to 0·75 toward the end of the process. The time required to deposit 0·35–0·45 gram of metal is from 20 to 35 minutes with an anodic rotation of about 800 revolutions per minute. Small quantities of hydrazine sulphate (0·5–0·6 gram) are added to reduce any antimonial salts which may be formed.

Bismuth.

Until the advent of rotating electrodes, and particularly of the method of graded potential, bismuth was one of the most difficult metals to deposit, since it almost invariably came

down in a powdery and non-adherent form. These remarks do not apply to the mercury cathode. According to Kollock and Smith (J. Amer. Chem. Soc. 27, 1539) to a solution containing about 0·2 gram of the metal as nitrate, the volume of which should not exceed 12 c.c., 0·5 c.c. of strong nitric acid is added. A current of about 4 amperes is passed, and the whole of the bismuth will be precipitated in from 12 to 15 minutes. The anode should be very rapidly rotated, so that the mercury may take up the bismuth as it separates, otherwise it may collect in a black mass beneath the anode.

Sand (Chem. Soc. Trans. 1907, 373) uses a solution containing tartaric acid; any excess of nitric acid, which may be in the original solution, is removed by the addition of sodium tartrate. By means of the auxiliary electrode, the cathode potential is maintained between 0·63 and 0·9 volt. The anode is rotated at 800 revolutions per minute. In one case the amount of metal in the solution was 0·2 gram, 2·5 c.c. of nitric acid (1 : 4) was added, and 8 grams of sodium tartrate. With a current varying from 0·2 to 3 amperes the metal was deposited in 9 minutes.

A. Fischer uses an electrolyte containing for each 0·5 gram metal, 10 grams of potassium oxalate, and 5 grams of Rochelle salt. By means of an auxiliary electrode, the cathode potential is kept at 0·8 volt. Temperature of solution, 75°; time required, 11 to 15 minutes.

Tin.

Tin can be satisfactorily deposited from an ammonium sulphide solution. Sodium sulphide is not satisfactory; indeed, tin is not thrown out from strong solutions at all. Hence, we have here a method of separation of antimony and tin. If the tin solution is acid, it is first neutralised with ammonia, and then sufficient yellow ammonium sulphide is added to dissolve the precipitate and form a clear solution. With stationary electrodes and a current of 1·0–1·8 amperes, the tin will be deposited in from 3 to 4 hours.

With rotating electrodes the metal can be deposited in from 15 to 35 minutes, depending upon the current employed, and the temperature of the electrolyte. Currents of from 1·8 to 8 amperes have been successfully employed.

A mercury cathode also gives very good results. The tin salt is dissolved in dilute sulphuric acid, and electrolysed with a current of from 2 to 5 amperes. From 0·5 to 0·8 gram can be deposited in from 8 to 12 minutes.

When platinum electrodes are employed, considerable difficulty may be experienced in removing the deposit. The simplest method is to make the electrode on which is the deposit, the cathode in dilute sulphuric acid, a piece of copper wire serving as cathode. Some workers prefer to coat the electrode with copper, and then the copper with tin, the tin being deposited from an ammonium oxalate solution; this proceeding, however, is tedious.

Tellurium.

Finely powdered tellurium is dissolved in a few c.c. of conc. sulphuric acid. The white anhydride so obtained is washed with a little freshly boiled water into the electrolysing vessel, and then 80 c.c. of a 10 p.c. solution of pyrophosphoric acid or sodium pyrophosphate added. The solution is then electrolysed with a C.D. of 0·1 ampere. Time of deposition, 4 to 5 hours. When a rotating electrode is employed, the time of deposition is much accelerated.

Group II.—Zinc.

Zinc is rather a difficult metal to deposit satisfactorily and quantitatively, and a very large number of methods have been suggested by different workers. Although it is +0·77 volt more positive than hydrogen, it can be deposited from slightly acid solutions, owing to the high supertension of hydrogen evolution from the surface of zinc, the supertension of hydrogen being 0·70 volt.

With zinc it is advisable always to employ rotating electrodes. The electrodes need not, however, be made of platinum; nickel, particularly in the form of gauze, answers equally well.

Price and Judge (Trans. Faraday Soc. 1907, 88) use an electrolyte containing sulphuric acid which must not be more than $\frac{1}{6}N$ and sodium sulphate.

It is, in fact, better to keep the normality of the acid rather lower than one-sixth. By starting with a C.D. of 0·25 ampere and increasing to 2·0 amperes about 0·2 gram of metal can be deposited in 40 minutes.

Owing to acetic acid being much less dissociated than sulphuric acid, solutions containing considerable quantities of this acid may be used. Thus, Exner (J. Amer. Chem. Soc. 1903, 896) deposited 0·25 gram zinc with a current of 4 amperes in 15 minutes. The electrolyte contained 3 grams sodium acetate and 0·30 p.c. acetic acid. A. Fischer (Chem. Zeit. 1907, 25) takes 1 c.c. conc. sulphuric acid, 3·5 c.c. conc. ammonia, 1·5 c.c. acetic acid, and 2·5 grams ammonium acetate. A. Classen (Quant. Analyse d. Elektrochem. 1897, 156) uses a solution of potassium oxalate, the zinc solution is added to a solution of from 4 to 5 grams of potassium oxalate. As soon as the electrolysis has started, it is advisable to add a few c.c. of a 1 p.c. solution of oxalic acid. Ammonium salts must be absent.

Kollock and Smith use a mercury cathode, and a solution of zinc sulphate or zinc sulphate acidified with sulphuric acid.

Zinc adheres somewhat firmly to platinum electrodes, and, if left on for some time, seems to alloy with the electrodes. If, however, it is removed shortly after the electrolysis, no ill effect is produced. The best method to remove the deposit is to warm the electrode in a strong solution of sodium hydroxide.

Cadmium.

Although cadmium is electropositive to hydrogen by as much as 0·42 volt, yet, owing to the high supertension of hydrogen with this metal, it is possible to deposit it from acid solutions. Owing, however, to the depolarising action of nitric acid, nitrates should not be present; on the other hand, small amounts of chlorides do not seem to matter.

Cadmium may be deposited from solutions containing small quantities of free sulphuric acid. It is usually advisable to add, after the bulk of the cadmium has been deposited, the equivalent amount of sodium hydroxide to neutralise the sulphuric acid which has been set free through the deposition of the metal. In 100 c.c. of solution, 1 c.c. of concentrated

sulphuric acid may be added before commencing the electrolysis. With stationary electrodes and a current of 0·1 to 0·35 ampere, the metal is deposited in from 3 to 4 hours; with a rotating electrode and a current of 4 to 5 amperes, the deposition is complete in 20 minutes. The deposition from cyanide solutions is the simplest and most easy to carry out. A solution of potassium cyanide is added to the cadmium solution until the precipitate first produced is dissolved, and then about half the quantity already added is run in. It is advisable also to add about 2 c.c. of a normal solution of sodium hydroxide. With stationary electrodes and a current of 0·15–0·35 ampere at a temperature of 50°, the deposit is complete in from 4·5 to 5·5 hours; with rotating electrode and a current of from 5 to 8 amperes, in from 15 to 30 minutes.

GROUP III.—**Iron.**

It is not often that the analyst requires to deposit iron electrolytically, owing to the very satisfactory methods of titration and precipitation. Iron cannot be deposited from acid or even from neutral salt solution upon a platinum electrode, owing to its being so much more electropositive than hydrogen—0·34 volt, while the supertension of hydrogen is only 0·08 volt. Kollock and Smith (Proc. Amer. Phil. Soc. 44, 149, and 45, 261) have, however, succeeded in depositing iron from weak acid solutions by means of a mercury cathode, the iron as it is deposited amalgamating with the mercury. The method described by these authors is as follows:—

Five c.c. contained 0·2075 gram of iron. Three drops (40 drops=1 c.c.) of concentrated sulphuric acid were added to it, when it was electrolysed with a current of 3 to 4 amperes and 7 volts. The anode made from 500 to 900 revolutions per minute. The iron was completely deposited in 7 minutes. The water was then siphoned off and the amalgam washed, as in all previous cases, with alcohol and water.

From its oxalate, tartrate, or citrate solutions, iron may be satisfactorily deposited, but in all cases traces of carbon are deposited along with the metal. By employing low-current densities, the amount of carbon deposited from oxalate and tartrate solutions is negligible, but from citrates the results are almost always considerably too high.

Ammonium oxalate.—This method was first suggested by Classen (Zeit. f. Elektrochem. i. 288), and is the one most generally employed. The iron solution, which should be free from chlorides and nitrates, must be poured into the solution of ammonium oxalate, if it is in a ferrous condition, otherwise a precipitate of ferrous oxalate may be formed which is difficult to dissolve. With ferric salts the order of adding does not matter.

Dissolve 5–7 grams of ammonium oxalate or acid ammonium oxalate in a small quantity of hot water, and to this add the iron salt also dissolved in a little water. The solution is then made up to the required bulk, and electrolysed with a C.D. of from 0·6 to 1·2 amperes. Time of deposit from cold solutions and with stationary electrodes, 4 to 5 hours; from solutions at 50°–60°, in 2 to 2·5 hours. As the electrolysis proceeds, it will sometimes be noticed that a small quantity of ferric hydroxide separates. This is due to the solution becoming slightly alkaline, owing to the decomposition of the oxalate by the current. Should the hydroxide be thrown out, small quantities of oxalic acid must be added.

With rotating electrodes the time of electrolysis is from 14 to 20 minutes.

With tartrate solutions the results are equally good. The method of procedure is similar to that described for oxalates, ammonium tartrate being used in place of the oxalate. The advantage of the tartrate method is that ferric hydroxide is never deposited; consequently, it is not necessary to add tartaric acid, and thus less attention is required.

Nickel.

Nickel and cobalt are difficult to determine by general analytical methods, but they can both be readily and accurately analysed by electrochemical means.

Although many methods have been suggested for the deposition of nickel, few of these are of practical importance. Most of them depend upon the use of the salts of organic acids. In such cases there is a tendency for traces of carbon to be deposited with the metal. The most useful and generally applicable method for depositing nickel is that of Fresenius and Bergmann (Zeit. f. Anal. Chem. 33, 9), in which the double salts of potassium and nickel or ammonium sulphate together with excess of ammonia are used.

The nickel salt is dissolved in water and mixed with an aqueous solution of from 4 to 5 grams of ammonium sulphate, and from 30 to 35 c.c. of strong ammonia. If more than 1 gram of the nickel salt is employed, larger quantities of ammonia should be added. As, however, large quantities of strong ammonia are apt to contaminate the atmosphere, it is better to work with smaller quantities of nickel. Nitrates should be absent, as their presence considerably retards the rate of deposition. With a current of 1–1·5 ampere per sq. dcm., the metal will be deposited in from 2 to 2·5 hours; at a temperature of 50°–60°, the time will be from 1·5 to 2 hours; with rotating electrodes, in from 15 to 30 minutes, depending upon the conditions and the form of apparatus. The metal is usually deposited as a brilliant plating on the electrode. The deposit is at times somewhat difficult to remove, and, owing to its appearance being rather like polished platinum, it is not always easy to ascertain whether it has been completely dissolved off. The best method of removing the metal is to warm the electrode in moderately strong sulphuric or nitric acid.

Other methods employed are the double oxalate method of Classen and Von Reiss (Ber. 14, 1622); ammonia and ammonium borate, by F. M. Perkin and W. C. Prebble (Trans. Faraday Soc. 1904, 103). Kollock and Smith (Proc. Amer. Phil. Soc. 45, 262) have used a mercury cathode successfully, the time of deposition being from 7 to 20 minutes. An amalgam of 40 grams mercury and 1 gram nickel has the consistency of soft dough, and is bright in appearance.

Cobalt.

Cobalt may be deposited from an ammonium sulphate, ammonium hydroxide solution similar

to that used in the case of nickel. But as a rule the results obtained are too low, owing to the tendency for peroxide to be formed on the anode.

F. M. Perkin and W. C. Prebble (Trans. Faraday Soc. 1905, 103) use a solution containing dihydrogen sodium phosphate and phosphoric acid. The solution is made up by adding 2 c.c. of a 5 p.c. solution of phosphoric acid to the solution of the cobalt salt in 70–80 c.c. water and then 20–25 c.c. of a 10 p.c. solution of dihydrogen sodium phosphate. The electrolysis should be commenced cold with a current density of 0·2–0·3 ampere per sq. dcm.; after about 50 minutes the solution is warmed to 50° or 60°, and the current increased to 1·2 ampere. If, as often happens, some peroxide is deposited on the anode, it can be removed by the addition of 0·2–0·3 gram of hydroxylamine sulphate. After the solution has become colourless, about 1 c.c. of *N*/1-ammonia should be added. The time necessary with stationary electrodes is from 4 to 5 hours. The deposit is extremely bright, resembling polished platinum.

The only methods which have been tried with rotating electrodes are solutions containing ammonium acetate and *solutions with sodium* formate. With currents of 8 amperes, L. Kollock and E. F. Smith (J. Amer. Chem. Soc. 29, 797) succeeded in depositing 0·3 gram of cobalt in from 30 to 40 minutes.

GROUP IV.—**Lead.**

Owing to its ready oxidisability, it is difficult to deposit lead satisfactorily on the cathode. Except in cases of separation from other metals, indeed, it is of no advantage to deposit it at the cathode. Sand has, however, found it a convenient method to separate lead from cadmium and bismuth (Chem. Soc. Proc. 22, 43).

From dilute solutions of nitric acid lead is partially deposited as metal on the cathode, and partially as peroxide at the anode. It is therefore necessary to have about 20 c.c. of nitric acid (1 : 4) to every 100 c.c. of electrolyte. Arsenic, manganese, selenium, and bismuth should be absent, and according to Vortmann (Annalen, 351, 283), antimony, silver, mercury, zinc, iron, cobalt, aluminium, and the alkali metals also cause the results to be high. Chromic acid should also be absent, and phosphoric acid retards the deposition. The lead salt is dissolved in water, and from 25 to 30 c.c. of strong nitric acid added. The electrodes used, whether stationary or rotating, should be roughened by the sand blast. With stationary electrodes and a current of from 1·3 to 1·8 ampere at a temperature of 60°–70°, the deposition will be complete in from 1 to 1·5 hours. At the commencement of the electrolysis a yellowish deposit is obtained which becomes orange or red, and finally dark-brown or black.

With rotating electrodes, the time of deposition is from 10 to 25 minutes.

At the end of the electrolysis the electrode is well washed by placing it in hot water, then washed with alcohol and ether, and heated to 220° in the air-bath for an hour. It must be cooled in a desiccator; the weight of the deposit is multiplied by the factor 0·866.

The best method to remove the deposit from the electrode is to warm it with equal volumes of nitric acid and water to which 4–5 grams of glucose has been added.

Lead does not give satisfactory results with a mercury cathode.

Manganese.

Manganese can only be deposited as oxide at the anode. It is, however, much more difficult to deal with than lead, as the deposit is apt not to adhere well. It is absolutely essential to employ roughened electrodes. Mineral acids cannot be employed. The most satisfactory electrolyte is one containing ammonium acetate, and Engels (Zeit. Elektrochem. ii. 413) has shown that the addition of small quantities of chrome alum helps to cause the deposit to adhere more firmly, probably owing to a depolarising effect. The manganese salt is dissolved in 40–50 c.c. of water, 8–10 grams of ammonium acetate added, and the solution electrolysed at a temperature of 75°–80°, with a current of 0·6 to 1 ampere. The deposition will be complete in from 1·5 to 2 hours.

With rotating electrodes the time will be about 30 minutes. In this case it is as well to add 10 c.c. alcohol to prevent frothing (J. Koster, Zeit. f. Elektrochem. 10, 553).

The best way to ascertain if all the manganese has been deposited, is to employ the permanganate test. Withdraw 1 or 2 c.c. of the solution, add 3 c.c. conc. nitric acid, and about 1 gram of red lead. Boil for a minute or two and dilute. A pink colouration indicates that the whole of the manganese has not been removed.

When all the manganese has been deposited, the electrode is washed as usual, and then strongly heated in order to convert the hydrated manganese peroxide into trimanganese tetroxide Mn_3O_4. It is necessary to heat until the black deposit becomes a dull orange red. The weight of the deposit multiplied by 0·72 gives the weight of metallic manganese.

Chromium.

This metal cannot be deposited on the anode as peroxide; neither under ordinary conditions is it possible to obtain a cathode deposit. Kollock and Smith (Trans. Amer. Chem. Soc. 27, 1905, 1255) have succeeded in depositing it in the form of an amalgam by employing a mercury cathode. The electrolyte consisted of dilute sulphuric acid. With a current of 1–3 amperes 0·12 gram was deposited in 20 minutes. This method is useful for separating chromium from aluminium, which latter metal is not deposited as an amalgam.

Classen (Ber. xxvii. 2060) oxidises chromic salts to chromates in an ammonium oxalate solution. This method is useful for separating chromium from iron, nickel and cobalt, and in the analysis of chromium steels and of chrome iron ore. The chromic acid produced can be estimated iodometrically or by precipitation as lead or barium chromate.

The solution containing the iron and chromium salt has excess of ammonium oxalate added to it, and if free mineral acid is present is neutralised with ammonia. It is then electrolysed, when the iron is deposited at the cathode and the chromium oxidised to chromate. The iron, when deposited in presence of chromium salts, is usually very brilliant like polished platinum. When all the iron is deposited, the

solution is removed, the iron deposit dried and weighed, and the chromium determined. If the whole of the chromic salt has not been oxidised during the deposition of the iron, the solution is again electrolysed. By using a rotating anode it is possible to completely oxidise 0·15 gram of a chromic salt, such as $Cr_2(SO_4)_3$ or Cr_2Cl_6 in 90 minutes, the volume of the solution being 120 c.c. and the amount of ammonium oxalate 15 grams. The electrolyte should be heated to 80°, and a current of from 5 to 5·5 amperes employed (Elektronalytische Schnellmethoden, p. 180).

Uranium.

Uranium is deposited at the cathode as oxide from solutions containing acetic acid or ammonium carbonate. The deposit consists of $U_3O_4,3H_2O$. At the end of the operation this is heated strongly to convert it into U_3O_8.

Wherry and Smith (Trans. Amer. Chem. Soc. 29, 806), by using a rotating cathode and an electrolyte containing in 125 c.c. 2·5–5·5 gram sodium acetate, deposited 0·25 gram of uranium in from 15 to 30 minutes, the current employed being 3–5 amperes, the electrolyte being either cold or heated to 50°.

Molybdenum.

From solutions containing dilute sulphuric acid, molybdenum can be deposited as peroxide at the cathode, but the deposit cannot be weighed as such. Wherry and Smith (Trans. Amer. Chem. Soc. 29, 806), therefore, oxidise it by means of nitric acid and weigh as MoO_3.

Thallium.

Many methods have been suggested for the electrolytic analysis of thallium, but only one can be considered satisfactory, and that is, by using a mercury cathode. By depositing the metal into pure mercury, it is found that portions are lost on weighing; but if the mercury contains a small quantity of zinc, this is not the case. Smith recommends to deposit the zinc and mercury simultaneously. In order to do this a definite volume of zinc sulphate solution of known strength is added to the solution before electrolysis. The electrolyte consists of dilute sulphuric acid. The amount of zinc necessary to protect the thallium is very small, and need not be more than 0·001 gram. With a current of 5 amperes it is possible to deposit as much as 0·2 gram in about 10 minutes. It is, however, advisable to electrolyse for a longer time.

GROUP V.—**Sodium.**

E. F. Smith (Trans. Amer. Chem. Soc. 25, 1903, 890) was the first to show that the metals of the alkali group could be analysed electrolytically. The method is based on the removal of the halogen anion of the metal by causing it to unite with silver, the alkali metal remaining in the solution as hydroxide is determined by titration; by ascertaining the increase in weight of the silver anode, the halogen can be also determined.

An ingenious apparatus has been devised by Hildebrand (Trans. Amer. Chem. Soc. 29, 1907, 447) for the analysis of the cations of the alkali metals, and of barium and strontium; and at the same time of various anions. In principle the cell resembles that of the Castner-Kellner process employed in the manufacture of sodium hydroxide.

The outer cell (Fig. 68) consists of a crystallising dish, 11 cm. in diameter and about 5 cm. deep; a beaker 6 cm. in diameter and 4·5 cm. high, with the bottom cut off, is placed inside, and rests on a triangle of glass rod placed on the bottom of the crystallising dish. The beaker is kept in position in the middle of the dish by means of three rubber stoppers fitted radially between it and the outer dish. Two compartments are thus formed, which are sealed off by means of mercury. In the outer compartment there is a ring consisting of six turns of stout nickel wire, provided with three legs dipping into the mercury and serving to maintain the lowest winding of the nickel about 1 cm. above the surface of the mercury, when sufficient is placed in the dish to seal off the two compartments. By means of a platinum wire passing through a glass tube the mercury is made the cathode. The anode consists of two discs of platinum gauze heavily plated with silver.

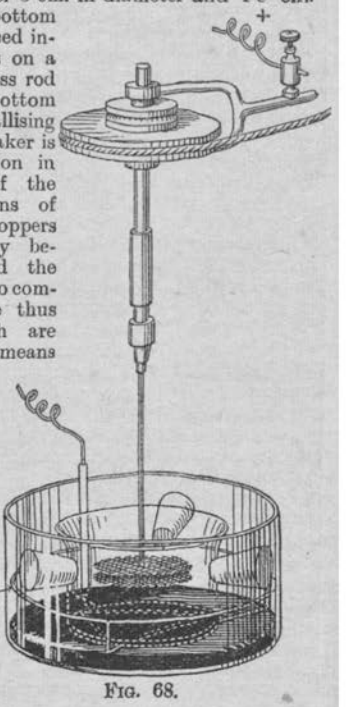


FIG. 68.

Pure mercury must be used, and the cell must be kept scrupulously clean. Before starting the cell, mercury is poured in so that its level is about 3 mm. above the lower edge of the inside beaker. The solution to be electrolysed is then put into the inner compartment. In the outer one enough distilled water to cover the nickel wire is placed, and to this 1 c.c. of a saturated solution of common salt. By this arrangement the amalgam formed in the inner compartment is immediately decomposed in the outer one. The sodium chloride serves merely to make the liquid a conductor, so that the action may proceed more rapidly at the commencement. Unless this is done, the amalgam is not entirely decomposed in the outer compartment, because pure water does not attack it rapidly enough to prevent the partial decomposition in the inside cell. After the electrolysis is complete, the entire contents of the cell are poured into a beaker, the cell rinsed, and the alkali titrated. After titration the mercury is washed, the water decanted, and the metal poured into a large separating funnel from which it can be drawn off clean and dry.

The table on p. 257 give the results which were obtained by Hildebrand.

The weighed gauze anode is clamped to the shaft. The latter is lowered into the cell till

the lower gauze is about 5 mm. from the surface of the mercury. The most convenient speed for the motor is about 300 revolutions per minute. The anode does not require washing, as the water after electrolysis is pure. It may be at once dried in the steam oven.

Time : Mins.	Volts	Amperes	Sodium in grams		Chlorine in grams	
			Present	Found	Present	Found
30	4·0–2·5	0·50–0·02	0·0461	0·0459	0·0708	0·0704
45	3·5–2·5	0·34–0·01	0·0461	—	0·0708	0·0706
40	3·5–3·0	0·50–0·01	0·0461	—	0·0708	0·0704
45	4·0–3·5	0·65–0·01	0·0461	—	0·0708	0·0716
30	4·0–2·5	0·76–0·02	0·0461	—	0·0708	0·0713
55	3·0	0·26–0·02	0·0461	—	0·0708	0·0709

By means of this apparatus the halogen salts of the alkali metals can be analysed. Also the halogen salts of barium and strontium. In fact, any anion with any metal which will unite with silver to form an insoluble salt can be analysed, provided, of course, that the metallic salt is soluble, and that the metal will form an amalgam with the mercury. In the case of the alkali metals and of strontium and barium, the hydroxides of which are soluble in water, the cations are analysed by titration. With other metals forming amalgams which are not readily decomposed this method of analysis is not to be recommended, because, in the first place, the considerable quantity of mercury necessary is inconvenient to weigh, and, secondly, it requires to be kept very pure, consequently the continual purification of such large quantities of mercury would be tiresome.

Analysis of anions when united with heavy metals. The SO_4 anion in such salts as copper sulphate may be analysed by electrolysing a known weight of copper sulphate dissolved in water with a mercury cathode and a platinum anode as already described. When all the copper has been deposited, the solution is siphoned off, the amalgam washed with water, and the wash water added to the original solution. The whole of the anode solution is then titrated with *N*-sodium hydroxide. The copper can, of course, be estimated by weighing the amalgam.

Separation of sodium from calcium and magnesium. When calcium and magnesium salts are electrolysed in Hildebrand's apparatus, it is found that the hydroxides of these metals are precipitated in the inner cell. It has therefore been found possible to separate sodium from these metals by means of this apparatus. The outer cell contains all the sodium as hydroxide, and the sodium can be determined by titration. The analytical results obtained are practically theoretical.

In a similar manner barium can be separated from calcium and magnesium.

Arsenic.

It is not possible to deposit arsenic quantitatively in the metalloid condition, neither can it be precipitated at the anode as oxide. Arsenic is readily converted by nascent hydrogen into arseniuretted hydrogen, its gaseous hydride, AsH_3; hence, electrolytic methods of analysis are not usually employed for analysing arsenic compounds. It is, however, possible to estimate very small quantities of arsenic contained in food, &c., by electrolysis. The process consists in evolving electrolytic hydrogen in presence of the arsenic, whereby the arsenic is converted into arseniuretted hydrogen. The gaseous hydride is then passed through a glass tube, heated by a small Bunsen burner, as in the Marsh apparatus, whereby the arsenic is deposited upon the tube in the form of a mirror. In order to estimate the amount of the arsenic, the mirror is then compared with mirrors prepared from known quantities of arsenic.

In 1812 Fischer (Gilbert's Ann. 42, 92) suggested the employment of the electric current to detect the presence of very small quantities of arsenic. It was again suggested by Bloxam (Quart. Journ. Chem. Soc. 1861, 13, 12 and 338) in 1861, but the apparatus had several disadvantages, and never came into practical use. Since then various modifications have been suggested by different authors, and, in 1903, Thorpe (Journ. Chem. Soc. 1903) describes a new form of apparatus which has been successfully employed for the analysis of traces of arsenic in food, beer, and other substances.

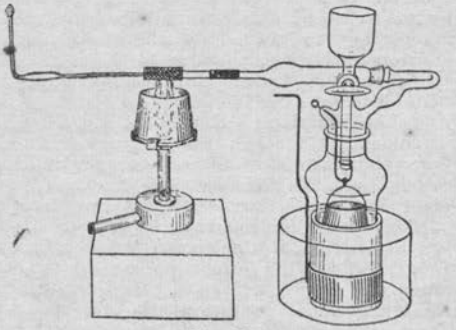


FIG. 69.

It consists of a platinum cathode hung in a glass cylindrical vessel, which is open at the end, and fits into a Pukal porous cell. The porous cell is surrounded by the anode, and stands in an outer vessel. The upper portion of the cylinder is open, and has a ground neck for the insertion of the drying tube filled with anhydrous calcium chloride, and also carries the funnel, which is fitted with a tap, through which the solution to be tested is run in. A capillary tube is connected to the end of the calcium chloride tube. The middle of this tube is heated by means of the small Bunsen burner, and is surrounded where the flame heats it with a piece of platinum or iron-wire gauze, to prevent the tube being fused. The whole apparatus is placed in a vessel containing cold water, to prevent undue heating during electrolysis.

Method of working. The apparatus is carefully washed with distilled water. The outer cell E is filled with dilute sulphuric acid (30 p.c.), then the inner cell. (The porous cell should be soaked in dilute sulphuric acid for about half an hour before being used.) As soon as all the connections are made, the Bunsen burner is placed in position, but not lighted, and the current is passed. A current of about 5 amperes should be used; the escaping hydrogen thereby

produces a flame of about 3 mm. in size. As soon as all the air has been driven out, which usually occupies about 10 minutes, the issuing hydrogen is ignited and the Bunsen burner lighted. If after about 15 minutes no brown ring makes its appearance, the reagents may be considered free from arsenic. At the end of 30 minutes the capillary tube is sealed off, and the open end also fused together. The mirror is then compared with the standard mirrors as above described.

Preparation of standard mirrors. Pure resublimed arsenious oxide is ground in an agate mortar and dried at 100°. Then 0·1 gram is carefully weighed and washed into a 1-litre flask, the flask being filled to the mark with distilled water. Each 1 c.c. of this solution contains 0·0001 arsenious oxide; 100 c.c. of this solution are diluted to 1 litre. This second solution contains 0·00001 gram of arsenious acid in each 1 c.c., or 0·01 mg. Standard tubes containing 0·004, 0·006, 0·008, 0·010, &c., mg. can then be prepared.

When foodstuffs are being examined for arsenic, Thorpe considers it advisable to take a portion of the foodstuff—arsenic free—and mix it with the known quantity of arsenic before proceeding to electrolyse it. The standard mirrors are thus prepared under the same conditions as those under which the suspected foodstuff is tested.

S. R. Trotman (J. Soc. Chem. Ind. 23, 177) recommends the adoption of a parchment membrane in place of the porous Pukal cell, as he considers this decreases the resistance, and thus makes the apparatus more sensitive. It is, however, not so convenient to use.

Sand and J. E. Hackford (Chem. Soc. Trans. 85, 1018) use the parchment membrane, but they also employ a heavy lead cathode and a lead anode. Their apparatus is thereby much cheaper than that used by Thorpe, and is said to be equally accurate.

Metallic Separations.

A large number of separations of metals by electrolytic methods have been worked out, but in many cases a purely chemical procedure or a combination of electrolytic and chemical methods is easier. There are, however, cases in which satisfactory and rapid electrolytic separations can be carried out. A few of the more important are given below.

Copper from nickel. By employing a rotating anode with an auxiliary electrode, and maintaining the cathode potential at 0·7–0·75 volt, copper can be deposited from solutions containing sulphuric acid. The solution is then made alkaline with ammonia, when the nickel can be deposited. If the cathode potential is not regulated, small quantities of the nickel are deposited along with the copper.

Exner (J. Amer. Chem. Soc. 25, 896) finds that by employing a solution containing nitric acid and ammonium nitrate (volume of solution 125 c.c.; HNO_3, 0.25 c.c.; 3 gram NH_4NO_3) and using a rotating anode, it is possible to deposit as much as 0·25 gram copper in 15–20 minutes; the nickel, which may be of equal weight, remains in solution, and can be afterwards deposited.

Copper from lead. Since lead is deposited from solutions containing nitric acid as peroxide on the anode, whilst copper is deposited as metal at the cathode, it might be supposed that there would be no difficulty in depositing both metals concurrently. It must, however, be remembered that unless there is a considerable concentration of nitric acid, a portion of the lead will be deposited as metal at the anode. On the other hand, in presence of copper, the tendency to reduction of the lead and its appearance at the cathode is decreased; that is to say, in presence of copper a lower concentration of nitric acid is required. It has, therefore, been found possible to separate the two metals. The volume of solution employed was 85 c.c., and contained 1 c.c. HNO_3 (1 : 4). With a rotating anode and a current of 2 amperes, the whole of the lead was deposited in 5 minutes. The current was then increased to 10 amperes, when the last traces of copper were removed. The washing and drying of the anode deposit requires care, since the peroxide when deposited from weak acid solutions does not adhere so well as from stronger solutions (Sand).

Copper and arsenic. McCay finds the following conditions give a satisfactory deposit of copper in presence of arsenic. The arsenic remaining in the solution cannot, however, be estimated electrolytically, unless present in very small quantities.

To the solution 20 c.c. ammonium hydroxide (sp. gr. 0·91) and 2·5 gram ammonium nitrate are added, the volume of solution being 125 c.c. The solution is then electrolysed at a temperature of 50°–60°, with 0·5 ampere per 100 sq. decm. of electrode surface. As much as 0·22 gram of copper will be deposited in 3 hours. With a rotating anode about 15 minutes are required. In this solution the arsenic should be present as arsenate. Copper and arsenic may also be separated electrolytically from solutions containing potassium cyanide. If acid, the solution is neutralised, and then sufficient potassium cyanide added to just redissolve the precipitate first produced. With a current 0·25–0·27 ampere, the whole of the copper is deposited in about three hours.

Antimony from tin. Tin can be quantitatively deposited from solutions containing excess of ammonium sulphide. It cannot, however, be deposited from solutions containing excess of sodium sulphide. Antimony, on the other hand, can be deposited from solutions containing excess of sodium sulphide. It is therefore possible to separate antimony from tin by adding excess of sodium sulphide to a solution containing the two metals. If the solution is acid, it is first made slightly alkaline with sodium hydroxide before the sodium sulphide is added. It is, however, better to first precipitate the two metals as sulphides, and then dissolve them in a concentrated solution of sodium sulphide. The tin should be in the stannic state. The solution is electrolysed at a temperature of 50°–60° with a current of from 0·2 to 0·9 ampere per sq. dcm. of electrode surface. In from 2 to 4 hours the whole of the antimony is deposited. It is, however, almost always contaminated with small quantities of tin.

In order to deposit the tin, the sodium sulphide must be decomposed. This is done by adding about 25 grams of ammonium sulphate,

and boiling until no more hydrogen sulphide is evolved. The tin is now deposited by electrolysing with a current density of from 0·3 to 0·5 amperes.

The best method of separating antimony and tin is that of Sand, by means of graded potential and a rapidly rotating anode (Chem. Soc. Trans. xciii. (2) 1908, 1572). From solutions containing strong sulphuric acid (1 : 1) antimony is deposited at an auxiliary potential of 0·65 volt when the temperature is kept above 100°, and a small quantity of hydrazine sulphate is added. Tin, on the other hand, under similar conditions, is not deposited below 0·8 volt. The method of procedure when dealing with alloys of antimony and tin is as follows:—

The alloy is dissolved in a mixture of 40 c.c. conc. sulphuric acid, 5 c.c. water, and 2 c.c. nitric acid (1 : 42); on heating to 180°–200° solution rapidly takes place. It is necessary to remove the nitric acid because it causes the formation of antimonic acid, which is only slowly reduced to the metallic state electrolytically. In order to decompose the nitric acid (nitrosulphonic acid), a current of 5 amperes is passed, and the liquid heated to 250°–270°. After the current has been passed for 5 to 10 minutes at the high temperature, it is stopped. The solution is cooled to 100°, and 0·5 gram of hydrazine sulphate added. (N.B.—The amount of hydrazine sulphate added should be equal to the weight of metal taken.)

The temperature is then raised to 300°. It is again cooled to 100°, when from 30 to 40 c.c. of water and another 0·5 gram of hydrazine sulphate are added.

The anode[1] is then rotated to ensure mixing of the solution, the temperature of which rises to about 120°. The analysis is now begun, the auxiliary potential having first been adjusted to 0·53–0·65 volt. The current will vary between 3–4 amperes, and, at the end of the electrolysis, will drop to 0·4–0·5 volt. Time of electrolysis from 20 to 30 minutes.

The tin is determined as follows: The solution after the antimony has been deposited is mixed with about 4 grams of oxalic acid, and is neutralised with strong ammonia. In order to prevent loss by spurting the electrodes are placed in position, the rotating stem being passed through a hole drilled in a clock glass. The ammonia is poured on the clock glass and runs down the stem of the electrode into the solution, the anode or inner electrode being at the same time rotated. Considerable ebullition ensues, but none of the liquid is spurted out. Exact neutralisation is ascertained by the use of methyl orange as indicator. Litmus cannot be employed, since its colloidal nature hinders the deposition of the tin. After neutralisation, 0·5–0·75 c.c. of sulphuric acid are added for every gram of oxalic acid previously added.

The solution is electrolysed at a temperature of 70° with a current of 3–4 amperes. Time of deposit, 60–80 minutes.

Silver and copper. (Smith and Frankel, Amer. Chem. J. 12, 104.) To a neutral solution of the silver and copper salt, add 2–3 grams of pure potassium cyanide. Electrolyse at a temperature of 65° with a current of 0·03–0·05 ampere, and maintain the potential at 1·1–1·6 volt. The silver will be completely deposited in from 4 to 5 hours. After the silver has been weighed, the electrode is replaced, the current and voltage increased, when the copper will be deposited.

Silver may also be separated from copper in ammoniacal solutions by using an auxiliary electrode, and keeping the potential below 0·5 volt.

Iron from other metals. Iron can readily be separated from aluminium, vanadium, glucinum, uranium, thorium, and many other metals with which it may be alloyed by dissolving in sulphuric acid, filtering from any residue, nearly neutralising with ammonia, and electrolysing with a mercury cathode.

Cadmium from zinc. These metals can be separated by means of graded potential. The solution is made up by adding first 2 c.c. of conc. sulphuric acid, then 3·33 grams of sodium hydroxide, and 1 c.c. of glacial acetic acid. The auxiliary electrode is kept at a potential of 1·15 –1·20 volts, and the solution electrolysed at a temperature of 30°. The whole of the cadmium will be deposited in 11–14 minutes. The potential is afterwards raised, when the zinc can be deposited in about 30 minutes.

Bibliography.—Electroanalysis, by Edgar Smith (P. Blakiston's Son & Co., Philadelphia); Practical Methods of Electrochemistry, by F. Mollwo Perkin (Longmans, Green, & Co., London); Elektroanalytische Schnellmethoden, by A. Fischer (Ferdinand Enke, Stuttgart); Quantitative Analyse durch Elektrolyse, by A. Classen (Julius Springer, Berlin); Analyse des Métaux par Électrolyse, by A. Holland et L. Bertiaux (H. Dunod et E. Pinat, Paris). F. M. P.

ANAMIRTA COCCULUS or **A. PANICULATA** (Colebr.). The former is the superseded name, and the latter the true name, of the Indian Menispermaceous liane, whose dried fruits (Grains of Paradise) are supplied under the name of *Cocculus indicus* (*v.* COCCULUS INDICUS).

ANANAS, OIL or **ESSENCE OF.** A solution of ethyl butyrate in 8 to 10 times its weight of alcohol. It possesses the odour of the pine-apple (*Ananas sativus* (Schult.)), and is employed in confectionery and perfumery; also to imitate the flavour of rum (Hofmann, Annalen, 81, 87).

ANANDONIS GREEN, *Hydrated chromium sesquioxide* (*v.* CHROMIUM).

ANASPALIN. Trade name for a form of wool-fat.

ANATASE or *Octahedrite.* One of the trimorphous forms of titanium dioxide (TiO_2) met with as crystallised minerals; the others being rutile and brookite. It is found as small, isolated crystals of a steel-blue or honey-yellow colour, in schistose rocks, particularly in the Alps. L. J. S.

ANCHIETA BARK. The root bark of *Anchietea salutaris* (A. St. Hil.), one of the Violaceæ, a bushy shrub growing at Rio de Janeiro. It contains *anchietine*, a substance crystallising in straw-coloured needles, having a nauseous taste. Used for syphilis and quinsy (Peckolt, Arch. Pharm. [2] 97, 271).

ANCHUSIN (*Alkannin*) *v.* ALKANNET.

ANDA-ASSU, OIL OF. An oil obtained from the seeds of *Joannesia Princeps* (Vell.), belonging to the Euphorbiaceæ, growing in Brazil. It is clear, slightly yellowish, odourless, with a taste

[1] After the metal has dissolved, the subsequent operations are carried out with the electrodes in position.

at first nauseating and then sweet. It solidifies at 8°, its sp.gr. at 18° is 0·9176 (Pharm. J. [3] 12, 380).

ANDAQUIES WAX *v.* WAXES.

ANDROGRAPHIS PANICULATA (Nees) or *Karyat*. An Indian plant; is used as a tonic, and is similar to quassia in its action.

ANDROPOGON OILS *v.* OILS, ESSENTIAL.

ANDROSIN *v.* GLUCOSIDES.

ANESIN (*Aneson*). An aqueous solution of acetonechloroform, having marked anæsthetic and hypnotic properties (Apoth. Zeit. 1897, 12, 608) (*v.* ACETONECHLOROFORM).

ANETHOL *v.* OILS, ESSENTIAL.

ANGELICA OIL *v.* OILS, ESSENTIAL.

ANGICO RESIN. A Brazilian gum obtained from *Piptadenia rigida* (Benth.) [*Acacia Angico*]; soluble in water and proof spirit. Used in chest complaints (Symes, Pharm. J. [3] 13, 213). Angico wood is that of another Brazilian leguminous plant, *Enterolobium ellipticum* (Benth).

ANGLESITE. Native lead sulphate ($PbSO_4$), forming brilliant, colourless, orthorhombic crystals, isomorphous with barytes ($BaSO_4$) and celestite ($SrSO_4$). It occurs in the upper oxidised zones of veins of lead ore, having resulted by the alteration of galena (PbS). It is less common than cerussite ($PbCO_3$), with

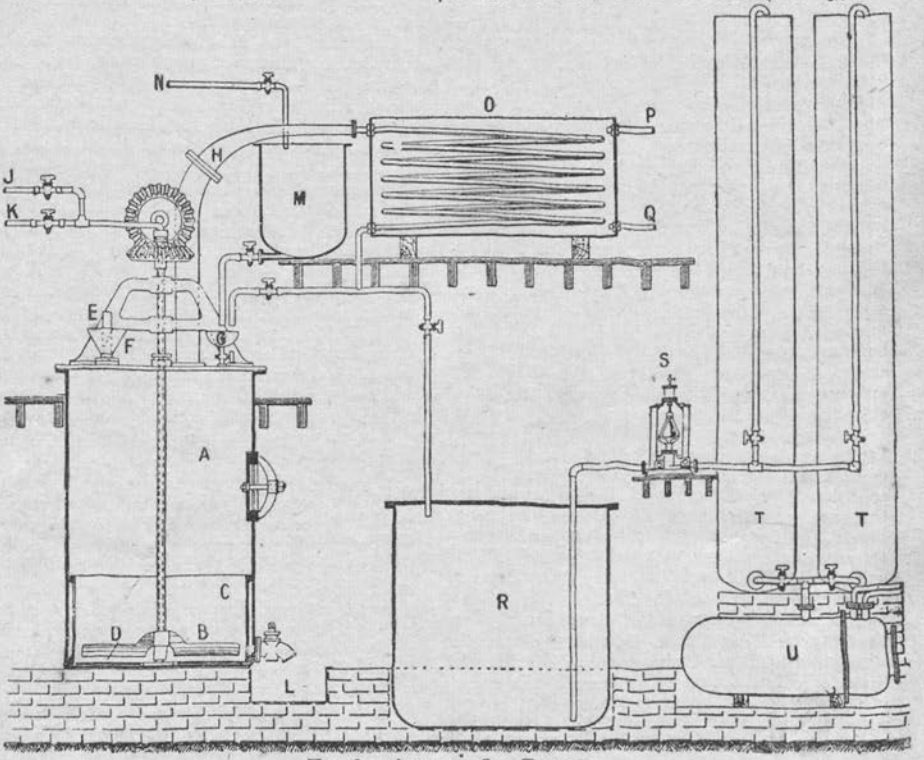


FIG. 1.—ANILINE OIL PLANT.

A, Aniline pan.
B, Agitating blades.
C, Side lining plates.
D, Bottom do.
E, Wood plug for hopper.
F, Feed hopper for borings.
G, Charging dish.
H, Vapour pipe to condenser.
J, Pure-steam pipe.
K, Aniline-steam do.
L, Gutter.
M, Receiving pan.
N, Pipe from N.B. tank.
O, Condenser.
P, Overflow.
Q, Cold-water inlet.
R, Receiver.
S, Steam pump.
T, Settling tubes.
U, Air pressure egg.

which it has sometimes been mined as an ore of lead. Good crystals have been found at many localities, perhaps most abundantly at Broken Hill, in New South Wales. The mineral takes its name from the Isle of Anglesey, where crystals were found by W. Withering, in 1783, in the Parys copper-mine. L. J. S.

ANGOSTURA BARK or **ANGUSTURA BARK** *v.* CUSPARIA BARK.

ANHYDRITE *v.* CALCIUM.

ANIL. The name of the American species of the indigo plant, *Indigofera anil* (Linn.).

ANILINE.

History.—First observed by Unverdorben in 1826 among the products of the destructive distillation of indigo. Detected by Runge in coal tar in 1834, and by Fritzsche in 1840, among the products obtained by distilling indigo with alkali hydroxides. Prepared by Zinin in 1840, by the reduction of Mitscherlich's nitrobenzene with hydrogen sulphide. Unverdorben called his product *krystallin*; Runge, *kyanol*; Fritzsche, *anilin*; Zinin, *benzidam*.

In 1843 Hofmann showed that nitrobenzene could be reduced by a metal such as zinc in the presence of a dilute acid, and also that krystallin, kyanol, anilin, and benzidam were identical with each other. Shortly afterwards Béchamp stated that nitrobenzene could be reduced by ferrous acetate in the presence of water, but that the oxalate, sulphate, &c., had no effect.

In the year 1856 Perkin's discovery of mauve

gave rise to a commercial demand for aniline, and the manufacture was commenced by Messrs. Simpson & Maule.

Preparation.—Benzene, then only obtained in small quantities and with much difficulty, as the treatment of tar scarcely existed, was introduced into glass balloons (known as 'bolt heads') of 1 gallon capacity, and the calculated quantity of nitric acid, mixed with about an equal volume of sulphuric acid, was gradually added, the mixture swung round and well agitated, and then allowed to stand. It was usual to have about twenty balloons in a row, and to add acid in turn until the reaction was complete.

The nitrobenzene was separated, washed, and reduced with iron borings and acetic acid, at first in a copper still, later in an iron cylinder. The aniline was freed from water, rectified, and was then ready for use. The selling price was about a guinea a pound.

Somewhat later cast-iron cylinders of considerable size were used for the reduction, acetic acid being still used and neutralised with soda or lime at the end of the reaction, and the aniline was in some factories distilled off over a naked fire, in others steam was blown into the mixture, and the aniline and water condensed and separated. Acetic acid continued to be used until about 1866. Since that time the apparatus has undergone little change, the treatment consisting in reduction mainly by the use of iron and water, hydrochloric acid being employed to start the reaction.

The aniline machine shown in Fig. 1 is the type that gives the best results.[1] A careful comparison between this design and the horizontal machine has proved unmistakably that the vertical machine is more economical and better in every respect. This is particularly the case with regard to repairs and maintenance. The machine is of cast-iron, 1⅛ inches thick, with driving gear, agitating shaft, and blades, as shown in the sketch. An important feature is the renewable cast-iron lining plates at the sides and bottom, which protect the machine from the friction caused by the revolving mass of iron borings. It is 6 feet 6 inches deep, and 4 feet 6 inches in diameter, having a total capacity of 650 gallons. Steam is admitted through the vertical shaft, which is hollow, and passes through the extremities of the horizontal agitating blades. Twenty-one of these machines are required to produce 150 tons of aniline oil per month.[2] A charge of 1000 lbs. of nitrobenzene is run into the receiving pan above the machine. To start the reaction, 1 cwt. of clean cast-iron borings, 10 gallons of hydrochloric acid, and 6 gallons of water are run in through the funnel-shaped hopper, and simultaneously steam is turned on and the nitrobenzene run in a thin stream into the dish on the top of the machine. The wooden plug in the hopper is driven in tight, and the space between it and the hopper is kept full of iron borings. By dexterously manipulating the wood plug, the borings can be added without allowing any vapour to escape. This simple method of 'feeding' the iron borings has proved better than many of the mechanical feeding devices that have been tried. Distillation proceeds, and the distillate passes through the condenser and runs back into the dish, together with the nitrobenzene which is carried over. The iron borings and nitrobenzene are added only in sufficient quantities to maintain a constant level in the dish. If the reaction proceeds too violently, loss is caused by the formation of benzene. When the level of the liquid in the dish begins to lower, the supply of nitrobenzene and iron borings is increased. This process is continued until the whole charge of nitrobenzene is run in, which takes about 10 hours. The total weight of iron borings required is 9 cwt. A sample caught as it runs from the condenser should then be quite free from nitrobenzene, and the machine will contain only aniline oil, water, and oxide of iron. The supply of steam is then increased, so as to distil over the aniline oil and water,[1] and the distillate is diverted into the tank beneath the condenser. The steam used for this distillation is not pure steam, but is generated from the aniline water mentioned below, in a separate boiler. The aniline water is that which separates from the oil in the separating tubes, and contains about 2 p.c. of aniline oil in solution. The aniline and water in the tank below the condenser are pumped into the settling tubes, and allowed to settle for 48 hours. The distillation of the oil and water from the machine takes about 7 hours, and during the last hour pure steam is again used, so that when the operation is finished, the condensed water left in the machine will be free from aniline, and can be used for flushing out the oxide of iron into the gutter which runs to the settling tanks outside. The oxide, after the water is drained off, is dried and ground, and disposed of for the purification of coal gas from sulphur. Large quantities are also now being used in the manufacture of cheap black paints, and the consumption in this direction is increasing. The aniline oil which has settled to the bottom of the settling tubes is run off into the air-pressure egg below, and blown into the crude aniline-oil store tanks, ready for the final purification by distillation in the vacuum still. The upper layer of water left in the settling tubes, and which contains about 2 p.c. of aniline in solution, is, as already explained, used for feeding the aniline steam boiler. The average yield of crude aniline oil from each machine, with a charge of 1000 lbs. of nitrobenzene, is 765 lbs. The yield of pure aniline oil from nitrobenzene is given further on.

The final purification of the crude aniline oil is done in a vacuum still. The sketch (Fig. 2) shows one of these stills of recent design. The body of the still is wrought-iron, 15 feet long, and 7 feet 6 inches in diameter, having a total capacity of 4000 gallons, and capable of distilling 35,000 lbs. in one charge. The steam is supplied from a boiler having a working pressure of 100 lbs. per sq. inch, at which pressure the steam possesses a temperature of 170°.

[1] See Chem. Trade J. 1906, 38, 59. The writer is indebted to Messrs. Davis Bros. for permission to reproduce the two figures.

[2] Larger machines, on the same principle, in which several tons of nitrobenzene can be reduced, are used by some manufacturers.

[1] In some works this distillation is not done, but the contents of the reduction apparatus are passed immediately through a filter press, the filtrate then running directly or being pumped into the settling tanks.

The internal steam tubes are wrought-iron, 2 inches in diameter. In place of the usual straight tubes which used to be expanded into both end plates, bent tubes are employed, which enter and return to the same end of the still. This prevents the 'tearing' of the tubes owing to expansion and contraction, and the 'breathing' of the end plates. The 'column' is of cast iron, 18 feet high and 9 inches in diameter. The condensing coils consist of three vertical flat copper coils, 2 inches in diameter, arranged side by side in a wrought-iron tank, the distillate entering all the three coils simultaneously from the still head by means of branch pipes. The total length of copper pipe in the condenser is 432 feet. The two receivers permit continuous working, so that when the first is full, as indicated by the gauge-glass tube, it is shut off, and the second brought into use. The contents of the first can then be drawn off while the second is being filled, and the vacuum is thus maintained throughout.

The still is charged with 35,000 lbs. of crude aniline oil from the store tank, and steam is turned on. The first fraction, about 7 p.c. of the distillate, consists of aniline oil and water, which is added to the crude oil and water in the separating tubes. The next fraction is 'light aniline,' and consists of aniline oil with a small quantity of benzene. If the reduction of the

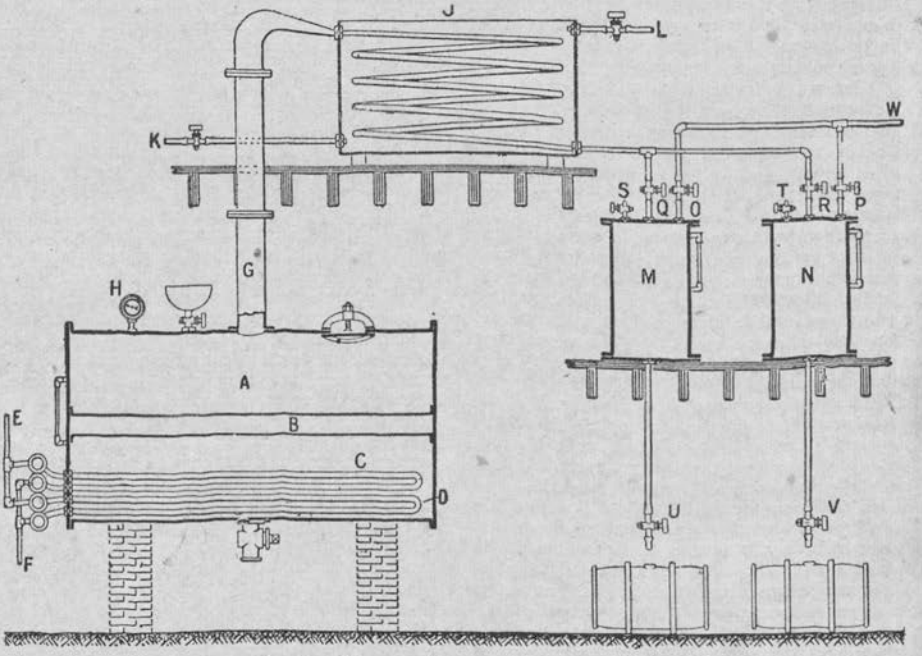


FIG. 2.—VACUUM STILL FOR ANILINE OIL.

A, Vacuum still.
B, Internal hollow stay.
C, Steam tubes.
D, Do. do.
E, Steam inlet.
F, Do. outlet.
G, Vapour pipe to condenser.
H, Pressure gauge.
J, Condenser.
K, Cold-water inlet.
L, Overflow for water.
M, Receiver for distilled oil.
N, Do. do. do.
O, Connection from vacuum pump.
P, Do. do. do.
Q, Inlet from condenser.
R, Inlet from condenser.
S, Air-admission tap.
T, Do. do.
U, Run-off tap for distilled oil.
V, Do. do. do.
W, Connection from vacuum pump

nitrobenzene has been carefully performed, this fraction is only about 4 p.c. of the distillate. It is collected and redistilled, giving pure aniline and benzene, the latter being returned to the nitrobenzene department, to be renitrified. The next fraction is pure aniline oil of marketable quality, clear and water-white. The tail end, called 'last runnings,' forms about 5 p.c. of the distillate, and, on redistillation, yields 80 p.c. of pure marketable aniline oil. The total yield of pure aniline oil obtained from nitrobenzene is 71¾ p.c. As the pure benzene yields 154½ p.c. of nitrobenzene, and the latter 71¾ p.c. of pure aniline oil, the total yield of pure aniline oil from pure benzene is 110·85 p.c. Compared with theory, there is little room for improvement.

The process of reduction and rectification as described applies also to toluidine, and modifications of the process are also in use for the production of xylidine and alphanaphthylamine, and of the reduction portion for the manufacture of metaphenylene- and metatolylene-diamine from the respective dinitro- compounds.

Valuation of Commercial Aniline Oil.

Aniline oil, as it occurs in commerce, may contain as impurities water, traces of insoluble hydrocarbons and of orthotoluidine, sometimes traces of hydrogen sulphide, and, if carelessly made, of nitrobenzene, benzene, and ammonia. Besides these, which should be carefully tested for, there is possibly a certain amount of aminothiophen, which has no deleterious action for

most, if not all, of the purposes for which aniline is used, and which, moreover, for the present at least, cannot readily be got rid of.

The method of testing usually adopted is to determine the boiling-point of the sample. For this purpose 100 c.c. are introduced into a small boiling flask with side tube, and distilled through a short condenser into a graduated 100 c.c. cylinder. Readings of the thermometer are taken as each 10 c.c. of the cylinder fills, and the last when 95 c.c. are filled. An alternative method is to take readings of the cylinder at each fifth of a degree rise of the thermometer. It is also usual to note the temperature when the first drop has fallen from the condenser. The thermometer readings should be corrected for barometer and immersion of mercurial column in the vapour of the liquid, and of course for the errors peculiar to the thermometer in use.

A few fragments of platinum wire, fire-brick, or wrought iron, should be placed on the bottom of the flask, and great care used to adjust the size of the flame and rate of boiling. The flask also should be held by the neck in a good clip over the naked flame, gauze being apt to cause currents of heated gas to flow up round the neck of the flask and superheat the vapour.

The specific gravity of the sample may also be taken (pure aniline has a specific gravity of 1·0265–1·0267 at 15°), although this indication is not of great moment if the boiling-points are good.

A recent example of the determination of the boiling-point is the following (Walter, Chem. Zeit. 1910, 34, 702):—

Temperature	P.c. over	Temperature	P.c. over
182·4°	3	183·2°	20
182·6°	4	183·4°	97
182·8°	5·5	183·6°	98
183·0°	11	183·8°	99

Pure aniline may be tested for insoluble oils by dissolving 10 c.c. in 40 c.c. of hydrochloric acid and 50 c.c. of water. The solution should be quite clear.

If, in carrying out the boiling test, the temperature rises considerably at the end, the presence of toluidine may be suspected. This can be detected when a considerable quantity of commercial pure aniline is made into acetanilide. On recrystallising this and working up the mother liquors, a small quantity of impure acetyl compound of low melting-point will always be found in the most soluble portion, or first mother liquors.

Nitrobenzene shows itself with the insoluble hydrocarbons. A very delicate test for it is to shake the sample of aniline violently for a few minutes, and then to notice the colour of the froth. The merest trace of nitrobenzene colours it a very distinct yellow.

The presence of water may be detected by distilling the sample (100 c.c.) as for a boiling-point determination, and collecting the first 10 c.c. in a narrow graduated cylinder of 15 c.c. capacity, shaking with 1 c.c. of saturated sodium chloride solution, and reading off the volume of the latter. The method will not show the presence of less than 0·3 p.c. of water, consequently, 0·3 c.c. must always be added to the amount of salt solution observed. It is not usual for aniline, sold as pure, to contain more than 0·5 p.c. of water.

Toluidine liquid should boil at 197°–198°, show a sp.gr. of about 1·000, and contain 30–40 p.c. para-, the rest ortho- toluidine.

Orthotoluidine. The sp.gr. of commercial orthotoluidine should be about 1·0037; b.p. about 197°–198°; should not solidify on cooling to −4°. Lunge (Chem. Ind. 1885, 8, 74) has published a table showing the specific gravities of mixtures of *o*- and *p*-toluidine.

For the estimation of small amounts of *p*-toluidine in *o*-toluidine, Schoen's method is perhaps the best. A standard oil is prepared, containing 8 p.c. of *p*-toluidine and 92 p.c. of *o*-toluidine, 1 c.c. of which is dissolved with 2 c.c. of pure hydrochloric acid in 50 c.c. of water, and oxidised cold by adding 1 c.c. of a saturated solution of potassium dichromate. After standing for two hours, the product is filtered, the precipitate being washed with water, and the filtrate and washings made up to 100 c.c. The toluidine to be tested is treated in the same manner, and compared colorimetrically with the above solution. J. C. C.

ANILINE BLACK *v.* DYEING.

ANILINE BLUE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ANILINE BROWN *v.* AZO- COLOURING MATTERS.

ANILINE SALT. The commercial name of aniline hydrochloride $C_6H_5{\cdot}NH_2{,}HCl$.

It is prepared in large quantities for the use of calico-printers, who employ it in the production of aniline black. The process consists in mixing the calculated quantities of pure aniline and hydrochloric acid in lead-lined or nickel-lined tanks, and allowing the salt to crystallise, freeing it from mother liquors in a centrifugal machine, and drying at a low temperature. The hydrochloric acid used should be of good quality, free from iron and even from traces of copper, or the salt will rapidly blacken.

The mother liquors may be neutralised with lime or soda, and the aniline recovered, or they may be boiled down and used in making magenta by the nitrobenzene process, &c.

'Aniline salt' occurs in commerce in large, white, nacreous and much-contorted plates.

The great desiderata for the calico-printer are that the salt should be made from pure aniline and should be dry and normal, containing 93 parts of aniline to 36·5 parts of hydrochloric acid; it should be free from sand and grit, which injure the printing machines. J. C. C.

ANILINE YELLOW *v.* AZO- COLOURING MATTERS.

ANIMAL CHARCOAL. (*Noir d'os*, Fr.; *Knochenschwarz*, Ger.) This substance, also known by the name of Bone Black or technically as 'Char,' is formed by carbonising bones at a high temperature in vessels from which air is excluded. Animal charcoal possesses the property of absorbing organic colouring matters from solutions brought in contact with it; thus a solution of brown sugar passed through animal charcoal will be found to have its colour more or less removed. This property is also possessed, though to a far smaller degree, by wood charcoal, as was first noticed by Löwitz about the year 1800. In fact, from that date to 1811, wood charcoal was much employed for

decolourising syrups, but it was then demonstrated by Figuier that bone black was far more effectual and energetic in its action.

In 1812 Louis Constant took out a patent for improving wood charcoal by washing and grinding, and using this prepared charcoal in sugar-refining.

In 1815 Messrs. P. & J. Martineau patented the use of animal charcoal, 'that is to say, animal substances properly burnt, charred, or calcined,' for refining and clarifying sugar; and in 1817 De Cavaillon in a patent, states that he had found that animal charcoal, after it has been used and again calcined, answers for the purpose of bleaching and clarifying sugar in 'a manner superior to new charcoal, and the operation may be repeated any number of times with equal effect.'

In 1830 Charles Derosne described the use of animal charcoal 'reduced to the size of fine gunpowder,' placed on a cloth in a layer to the height of 16 inches, and covered with a perforated diaphragm, as a filter for sugar solutions.

Although the effect of animal charcoal is most conspicuous in removing organic colouring matters from solution, it is also capable of absorbing many other organic and also mineral substances. It was proved by Graham that various mineral substances were removed from solution by animal charcoal; thus the lime is taken up from lime water, and metallic salts are absorbed from their solutions in water. According to Chevallier, lead nitrate and acetate are completely removed by animal charcoal. Weppen has shown that this action extends to a great variety of metallic salts, including cupric, zinc, chromic and ferrous sulphates, nickel, cobalt, silver, mercurous and mercuric nitrates, tartar emetic, stannous chloride, and ferric acetate.

As the result of a number of experiments on the absorption of different salts by animal charcoal, Bodenbender (The Sugar Cane, ii. 316) arrived at the following conclusions:—

1. The power which it possesses of absorbing salts is for the most part a physical property.

2. A given weight absorbs a larger proportion of salts from a concentrated than from a diluted solution; on the other hand, the proportion absorbed from a constant quantity of salts is more considerable when this quantity is in a dilute, than when it is in a concentrated, solution.

3. The presence of sugar has only a slight influence on the absorption of salts.

4. The salts of potassium are retained in smaller proportion than those of sodium.

5. Among the salts experimented with, the amount taken up is in the following order, beginning with that least absorbed: potassium chloride, sodium chloride, potassium nitrate, sodium nitrate, potassium acetate, sodium acetate, potassium sulphate, sodium sulphate, magnesium sulphate, potassium carbonate, sodium carbonate, sodium phosphate.

6. A chemical action of charcoal has been observed with respect to some carbonates, oxalates, and other salts, being brought about by the presence of calcium sulphate and phosphate in the charcoal.

7. Charcoal saturated with one salt is capable, within certain limits, of withdrawing another salt from solution.

8. There is less absorption by charcoal of a salt when in contact with it for a short time, than when the contact is prolonged. The difference due to time of contact, however, ceases when the contact has lasted some hours.

Various explanations have been offered to account for the peculiar action of charcoal. It was attributed by Bussy to the highly divided state of the carbon contained in it. From the similarity of the action of charcoal upon diverse bodies, and the general nature of its operation, it would appear to be due to some physical or mechanical cause. Charcoal seems, indeed, to exert merely a surface action, withdrawing the colour from the liquid passed through it, but not in any way destroying the same, and Kohlrausch has shown by experiment that by means of a solution of ammonia it is possible to practically dissolve out all the colour which has been absorbed by charcoal through which molasses has been previously passed.

In connection with the action of animal charcoal, it is stated by P. Degener and J. Lack (D. R. P. 31358, 1884) that the freshly ignited charcoal, moistened with as much water as it can take up, and exposed to light and air, produces, even in a few minutes, a perceptible quantity of hydrogen peroxide, and is thus rendered more active than the untreated material.

They also state that exposure for 48 hours in layers of 3 inches thick, the charcoal being frequently sprinkled with water and turned over gives good results, and that if milk of lime is sprinkled over bone black, calcium peroxide is produced, and in the same way other alkaline earths and alkalis can be converted into peroxides.

It was first observed by Tilliot that more organic matter is absorbed by charcoal from solutions at a high temperature than in the cold, this result being only partially due to the increased circulation caused by heating.

Manufacture of animal charcoal. The bones employed should be carefully selected, hard, and free from extraneous matter. Whale and fish bones are not of a suitable character, as they yield a soft char. Bones which have been exposed to atmospheric action for a long time, or which have been buried in the ground, cannot be successfully employed, as, owing to the alteration in their composition, they produce a char deficient in carbon.

Before proceeding to carbonise the bones, the fat is removed by boiling, or by means of a suitable solvent such as benzene. By the first-named treatment from 4 to 5 p.c. of fat is extracted, and by the second from 8 to 12 p.c. In the process of extracting fat from bones by means of a solvent, difficulties arise from the presence of water, and F. Seltsam (Eng. Pat. 10208, 1855) has proposed to overcome these by using a solvent (such as a hydrocarbon from petroleum) having a higher boiling-point than that of water, the temperature during extraction being raised to above 100°C. He states that by this means the water is expelled from the bones and the extraction of fat is rendered more complete. Lorenz says that bones after treatment with benzene contain 1·2–2·5 p.c. of fat, which can be extracted by a further treatment with benzene, and 0·48–0·8 p.c. of fat removable by ether, or in all, 1·68–3·3 p.c., which is lost in the process. This mode of extracting fat is employed in many factories on the Continent, and until recently was used in the United Kingdom,

but it is objectionable on the ground that the advantage gained in the increased amount of fat recovered is more than counterbalanced by the decreased value of the resulting animal charcoal.

The apparatus employed in making bone charcoal is similar to that used in a gasworks. The bones are carbonised, after being roughly crushed, in vertical or horizontal iron retorts of a round, oval, or D section, the latter by preference. The length of the horizontal retort is usually from 8 to 10 feet, the long diameter being 18 inches and the short diameter of the oval retort 12 inches. There are usually five or seven retorts in each bed. The retorts are connected in the same way as gas retorts, with a hydraulic main, and this again with condensers or scrubbers filled with coke in which the bone oil separates and from which the gases are exhausted. The gases are then forced through a series of washers containing water to remove the ammonia, the residual gases, which are employed for heating and lighting purposes, finally passing into a gas-holder. Charges of about 2½ cwt. of bones are carbonised in vertical, and 5 cwt. in horizontal retorts, the operation taking about 6 to 8 hours with the former and 8 to 10 hours with the latter. The bone oil collected in the condenser amounts to from 3 to 5 p.c. on the bones carbonised, and the ammonia in the ammoniacal liquor is equal to about 8 p.c. of ammonium sulphate, into which it is converted in the usual way. When the bones are completely carbonised the charcoal is removed from the retorts and cooled in strong sheet-iron canisters, which are at once covered with closely fitting lids and luted round the edges, either with charcoal paste or a water lute. The char when quite cold is crushed in a suitable mill (on its way to which any iron it may contain is removed by passing over the poles of an electromagnet), and then sifted into various sizes to suit the requirements of the sugar-refiner. It is usually moistened before grinding to keep down the dust. Good bones yield about 65 p.c. of char, but from 20 to 30 p.c. of this is dust, which fetches a lower price than the larger grist.

The following analysis gives approximately the composition of a good sample of new bone charcoal:—

Carbon	10·51
Calcium and magnesium phosphates, calcium fluoride, &c.	81·21
Calcium carbonate	7·30
Calcium sulphate	0·17
Ferric oxide	0·12
Silica	0·34
Alkaline salts	0·35
	100·00
Moisture originally present	8·00

Space occupied by one ton, 48 cubic feet.

Sizes left on sieves of various degrees of fineness:—

Above 10 holes to linear inch	0
10 to 20 „ „ „	28
20 to 30 „ „ „	32
30 to 40 „ „ „	27
40 to 50 „ „ „	11
Through 50 „ „ or dust	2
	100

The carbon always contains a certain proportion of nitrogen amounting to about one-tenth of its weight; there is also a minute proportion of hydrogen present. The nitrogen continually becomes less and less whilst the bone charcoal is being used for sugar-refining.

When char is repeatedly reburned, it becomes less porous and shrinks in volume, so that a ton of char, which, when new, measures 48 to 54 cubic feet, may be reduced to as low as 28 cubic feet after being reburned many times, or, in other words, its apparent density may be nearly doubled.

Wallace has, however, shown that the real sp.gr. varies but little; thus, a new char occupying 50·6 cubic feet per ton, or having an apparent sp.gr. of 0·71, had a real sp.gr. of 2·822, whilst a moderately old sample, occupying 35 cubic feet per ton, or having an apparent sp.gr. of 1·03, had a real sp.gr. of 2·857, or only a trifle over that of the new.

Another proof that char loses its porosity to a considerable extent by long-continued use and reburning is afforded by the fact, pointed out by Wallace, that dry new char will absorb from 80 to 100 p.c. of its weight of water, whereas old char will only retain from 30 to 45 p.c.

New charcoal of good quality should, in the dry state, contain not less than 9 and not more than 11·5 p.c. of carbon. The silica should not exceed 0·5 p.c., the oxide of iron 0·15 p.c., the calcium sulphate 0·2 p.c., and the moisture 8 p.c. Its weight should not exceed 52 lbs. per cubic foot. It should be of a dull black colour, and, when incinerated, leave an ash of a uniform white or cream colour; the presence of grey or reddish particles indicates that the sample has been mixed with old charcoal. When brought in contact with the tongue, it should adhere to it somewhat strongly. The size of grain which it is desirable to have in new charcoal depends upon the use to which it is to be applied. Large-grain charcoal is preferable for strong liquors, such as the liquor used for washing loaf sugar. Refiners, as a rule, prefer small grain; if, however, it be very small, it impedes the passage of liquor and also gives considerable trouble in washing. Char may be used over and over again and sometimes lasts several years, being revivified each time after use by reburning in special kilns (*see* SUGAR). When, by continued use, it has practically lost its power of removing colour, it is known as spent char, and is then used as a manure, either as it is, or more generally after treatment with sulphuric acid, so as to form superphosphate of lime.

Animal charcoal dust is employed as a pigment after being finely ground either in a dry or wet state; it is also used in the manufacture of blacking (*q.v.*).

Ivory black consists of char in an exceedingly fine state of division.

Although the chief use for animal charcoal is in refining sugar, it is also employed for the purification of water, vegetable or mineral oils, paraffin, glycerol, and various other organic substances.

It is sometimes found necessary to use a more powerful decolourising agent than ordinary bone charcoal, and this is prepared by treating new animal charcoal with dilute hydrochloric acid to dissolve out the inorganic constituents,

leaving the carbon behind. This, when carefully washed and dried, forms a most valuable decolourising agent. N. Bros.

ANIMAL OILS and FATS *v.* Oils and fats.

ANIME and **ANIMI** *v.* Oleo-resins.

ANISEED. (*Anis*, Fr., Ger.) The fruit of the *Pimpinella Anisum* (Linn.), cultivated in Malta, Spain, and Germany. Used for the preparation of anise oil and cordials. Alcohol extracts 36·24 p.c. of this spice (Biechele, Pharm. J. [3] 10, 878).

ANISE CAMPHOR *v.* Camphors.

ANISE OIL. The essential oil of aniseed, obtained by distilling it with water. According to Landolph (Compt. rend. 81, 97; 82, 226), it contains 90 p.c. of *anethole*, boiling at 226°. Anethole, according to Perkin (Chem. Soc. Trans. 32, 668), is *p*-allylanisole $C_6H_4(OMe)CH:CH\cdot CH_3$; he obtained it by heating *p*-methoxyphenylcrotonic acid.

Anise oil is sometimes adulterated with fennel oil; this can be detected by heating the oil, when the fennel odour becomes perceptible.

Star anise oil has a similar colour and taste, but it does not solidify at 2° (*v.* Oils, Essential).

ANISIDINE. $NH_2\cdot C_6H_4\cdot OMe$. *Orthanisidine.* Obtained by the reduction of orthonitranisole with tin and hydrochloric acid or iron and hydrochloric acid (Meister, Lucius, and Bruning, D. R. P. 7217 of Dec. 3, 1878), is a colourless oil, which boils at 226·5° at 734 mm. pressure (Mühlhaüser, Annalen, 207, 239); at 225° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210), and has a sp.gr. 1·108 at 26°. When diazotised and treated with β-naphtholdisulphonic acid (R-acid), it yields *anisole-red* (*v.* Azo- colouring matters). A mixture of orthanisidine (2 mols.) and paraphenylenediamine (1 mol.) is converted, on oxidation with potassium dichromate, into a reddish colouring matter formerly employed under the name *safranisole* (Kalle & Co., D. R. P. 24229 of Oct. 27, 1882; expired March, 1885).

Paranisidine, obtained from paranitranisole by reduction with tin and hydrochloric acid, crystallises in prisms which melt at 55·5°–56·5° (Lossen, Annalen, 175, 324) and boil at 245°–246° (Salkowski, Ber. 7, 1009); 243° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210); *p*-anisidine, *o*-sulphonic acid, prepared by boiling the hydrogen sulphate of *p*-anisidine, when diazotised and coupled with β-naphthol, yields an azo-compound forming red lakes with baryta, alumina, &c. (Aktiengesellschaft für Anilin-Fabrikation, D. R. P. 14665).

Chloranisidine, when diazotised and coupled with β-naphthol, yields a red compound insoluble in water (Julius, Ludwigshafen and Jahrmaht, U.S. Pat. 695812); *p*- and *m*-nitroanisidine, when diazotised and coupled with β-naphthol, yield red and pink dyestuffs (Imray, Eng. Pat. 25756; J. Soc. Chem. Ind. 1898, 1039; and Freyss, J. Soc. Chem. Ind. 1901, 356); *o*-iodo-*p*-anisidine, when diazotised and treated with naphthol sulphonic acid, yields a red dye, similar to that obtained from *p*-anisidine (Reverdin, Ber. 29, 997).

Anisidine condenses with orthoformic ester, and the resulting compound is used as an anæsthetic (Goldschmidt, Eng. Pat. 9792; J. Soc. Chem. Ind. 1899, 606).

ANISOCHILUS CARNOSUS (Wall.). An Indian plant belonging to the Labiatæ and containing a volatile oil. Used in quinsy.

ANISOLE. *Anisoil*; *Methylphenyl ether* $C_6H_5\cdot O\cdot CH_3$.

Preparation.—Anisole can be obtained by distilling anisic acid or *o*-methoxybenzoic acid with baryta, or by heating potassium phenate with methyl iodide at 120° (Cahours, Ann. Chim. Phys. [3] 2, 274; 10, 353; 27, 439). It is prepared by passing a current of methyl chloride over dry sodium phenate heated at 190°–200° (Vincent, Bull. Soc. Chim. 40, 106), and by heating phenol with methyl alcohol and potassium bisulphate at 150°–160° (Act. Ges. für Anil.-Fabrik.; D. R. P. 23775). It has been synthesised by fusing sodium benzene sulphonate with sodium methoxide (Moureu, J. Pharm. Chim. 8, v. 211).

Properties.—It is a colourless ethereal liquid, which boils at 155°–155·5° at 762·3 mm. (Schiff, Annalen, 220, 105) at 153·9° (corr.) (Perkin, Chem. Soc. Trans. 69, 1240); melts at −37·8° (Von Schneider, Zeit. Phys. Chem. 19, 997) and has a specific gravity 0·991 at 15° (*v.* Oils, Essential).

ANISOMELES MALABARICA (R. Br.). A much-esteemed Indian plant belonging to the Labiatæ; an infusion of the leaves is used in intermittent fevers, and the essential oil is applied externally in rheumatism.

ANKOOL, AKOLA, DHERA BARK. The root bark of *Alangium Lamarckii* (Thw.), one of the Cornaceæ, used in leprosy and skin-diseases (Dymock, Pharm. J. [3] 9, 1017).

ANNATTO is derived from the fruit of the *Bixa orellana* (Linn.), a shrub found native in Central America, and cultivated in Brazil, Guiana, Mexico, the Antilles, and India.

To prepare the dyestuff, the seeds and pulp are removed from the mature fruit, macerated with water, and the mixture is left to ferment. The product is strained through a sieve, and the colouring matter which settles out is collected, partially evaporated by heat, then placed in boxes, and finally dried in the sun.

Annatto comes into the market in the form of cakes, and among the different varieties Cayenne annatto is the most esteemed, and is considered to be the richest in colouring matter. It should contain from 10 to 12 p.c. of the pure dye, and not more than 5 p.c. of ash, whereas the amount of colouring matter in the Bengal product is frequently lower than 6 p.c.

In 1848 Dumontal devised a new method for the preparation of annatto, in which fermentation is avoided, and the pulp is simply washed out from the capsules and off the seeds. The product known as *bixin* is said to be five to six times more valuable than ordinary annatto (Crookes, Dyeing and Calico-Printing).

The colouring matters of this dyestuff were first investigated by Chevreul (Leçons de chimie appliquée à la Teinture), who isolated two substances, one yellow, which was called *orrelline*, soluble in water, and a second, *bixin*, which is red and very sparingly soluble.

Bixin, the useful colouring matter, was subsequently examined by numerous chemists, who were only successful in preparing it as an amorphous powder, and its isolation in a crystalline condition was first achieved by Etti (Ber. 7, 446; 11, 864).

Etti digested 1·5 kilos of purified annatto

with a solution of 150 grams of calcined soda ash in 2·5 kilos. of 80 p.c. alcohol on the water-bath at 80°. The mixture was filtered and the residue pressed between warm plates, and again extracted with 1·5 kilos. of warm 60 p.c. alcohol.

The alcoholic filtrate was diluted with half its volume of water, concentrated sodium carbonate solution added, and the crystalline precipitate of sodium bixin was collected after several days, and pressed. The product purified by solution in 60 p.c. alcohol at 70°–80°, and reprecipitation with sodium carbonate was finally made into a cream with alcohol, and this, when neutralised with hydrochloric acid yielded crystalline bixin.

A simpler method has been more recently devised by Zwick (Ber. 30, 1972). Well-dried annatto is extracted for 24 hours with boiling chloroform, the extract evaporated, and the residue thoroughly exhausted with ligroin. The product is crystallised from chloroform, and after washing with ligroin, is repeatedly recrystallised from the former solvent.

Bixin $C_{28}H_{34}O_5$ (Etti, *l.c.*; Marchlewski and Matejko, Chem. Zentr. 1906, ii. 1265) consists of brown-red or deep-red rhombic crystals, which, when slowly heated, melt at 191·5°, and when rapidly heated, at 198°. It is sparingly soluble in the usual solvents, and of these it is most readily dissolved by chloroform or alcohol. Concentrated sulphuric acid dissolves bixin with a cornflower-blue colouration, and this reaction is characteristic, and is given by minute traces of the substance.

Monosodium bixin $C_{28}H_{33}O_5Na+2H_2O$ is best prepared by dissolving 10 grams of bixin in a solution of 1·2 grams of sodium carbonate in 300 c.c. of 12 p.c. alcohol at 70° (Etti, Zwick). It is deposited on cooling in dark-red iridescent crystals, and can be obtained in the anhydrous condition by recrystallisation from 70 p.c. alcohol (M. and M.).

Disodium bixin $C_{28}H_{32}O_5Na_2+2H_2O$ is obtained when 20 grams of bixin is dissolved in a solution of 10 grams sodium carbonate in 600 c.c. of boiling 12 p.c. alcohol. It consists of a dark-red amorphous powder (Etti). *Monopotassium bixin* $C_{28}H_{33}O_5K+2H_2O$ and *dipotassium bixin*, $C_{28}H_{32}O_5K_2+2H_2O$ have also been prepared.

Bixin contains one methoxyl group. Distilled with zinc-dust, bixin yields, according to Etti, *metaxylene*, *metaethylxylene*, and a hydrocarbon $C_{14}H_{14}$, b.p. 270°–280°.

According to Zwick, bixin is readily reduced by sodium amalgam, and a compound, $C_{23}H_{40}O_7$, is thus produced. Marchlewski and Matejko, on the other hand, studied the action of zinc-dust and acetic acid, and obtained in this manner an orange-coloured crystalline substance which possessed a strong metallic lustre. When slowly heated, it melts at 200·5°, but if the operation is carried out rapidly, at 208°–210°. This compound is evidently of an unstable nature, for whereas when freshly prepared it gives C=75·4, H=7·7 p.c., on standing for some days in the air it becomes colourless and then gives C=58·6, H=5·8 per cent. At 100° this change occurs more rapidly.

Dyeing properties.—Annatto is still employed to a fair extent for colouring oils and butter, but is almost extinct as a dyestuff in this country. As the orange-red colour which it yields is extremely fugitive to light it has at no time been very extensively used. On the other hand, it resists the action of soap and dilute acids very well.

In order to dye cotton, the annatto is first dissolved in a boiling solution of carbonate of soda, and the goods are then entered and left in the bath for a quarter of an hour. They are subsequently pressed out, and washed in slightly acidulated water or alum solution.

For silk, the bath is made up with equal parts of annatto and sodium carbonate; soap is also usually added, and the dyeing is continued at 50° for about an hour, according to the shade required. The colour produced can be rendered somewhat more yellow by passing the fabric through a weak solution of tartaric acid.

Wool is dyed at 80°–100°, without any addition to the bath. A. G. P.

ANNEALING. (*Le recuit*, Fr.; *das Anlassen*, Ger.) A process which is applied principally to glass and metals for the purpose of rendering them softer or less brittle. The process itself always consists in the application of heat for a period of time, which may vary from a few minutes to many hours, and which may be followed by very slow cooling; the object of the process is to permit the material to attain approximate equilibrium in regard to its internal structure. This state of normal internal equilibrium may be disturbed either by the effects of rapid cooling or by the application of mechanical deformation. The former is most frequently met with in glass, and in large metal castings, while the latter is found in 'wrought' metal of all kinds.

In the case of substances which are poor conductors of heat, such as glass, and also in masses of metal which are so large that thermal conductivity cannot produce reasonable uniformity of temperature, relatively rapid cooling sets up severe stresses, owing to the fact that the outer or most rapidly cooled layers solidify first; subsequently the internal portions of the mass endeavour to contract in solidifying, and in cooling, but find themselves constrained by their attachment to a relatively rigid external envelope; the tendency to thermal contraction is therefore overcome by severe tensional stresses. A body in this condition, while it may present the phenomenal strength of a 'Rupert's drop,' is liable to sudden fracture, particularly if the surface is cut or broken. In such substances, effective annealing implies heating to a point where the mass becomes sufficiently soft to release all internal stresses, followed by very slow cooling down to the temperature at which the body is completely solid. In the case of fine optical glass, the rate of cooling is retarded so that a fall of 100° occupies one week. For metals such excessively slow cooling is undesirable, and is never intentionally used.

Metals in the cast or other 'normal' condition consist of aggregates of minute crystals of approximately equal dimensions in all directions; when metal is mechanically deformed, as by hammering, rolling, or other working process carried on in the cold, these minute crystals are elongated in the same general sense as the mass of which they form part, and this

deformation of the crystals is accompanied by the well-known hardening of the metal under cold work. This is due in part to the internal rearrangement which each crystal undergoes, and in part to the partial and local destruction of the crystalline arrangement itself, accompanied by the formation of a hard amorphous 'phase' (Ewing and Rosenhain, Phil. Trans. 1899, ser. A, cxiii. 353–375; Beilby, Phil. Mag. 1894). When the metal is subsequently annealed, *i.e.* heated to a suitable temperature, the metal 'recrystallises,' the crystals rearrange themselves, and the original condition is approximately restored. In some metals the molecular mobility is such that recrystallisation takes place slowly even at the ordinary temperature (lead: Ewing and Rosenhain, Phil. Trans. 1900, cxcv. 279–301; brass: Cohen, Rev. general des Sciences, April 30, 1910); but in the greater number of cases a high temperature is required. In the great majority of pure metals, and in some alloys, the rate of subsequent cooling is immaterial so far as the softening effect is concerned; but in certain metals and in a large number of alloys either allotropic or other changes take place during gradual cooling, and these transformations are more or less inhibited by rapid cooling; in such metals the rate of cooling through the 'critical temperatures' at which these changes occur is of material importance. The most striking example is found in carbon steels, which are moderately soft if cooled slowly down to a temperature of 650°, but become exceedingly hard if suddenly cooled from a temperature above 700°. In the case of hardened tool steel, the process of annealing consists in raising the steel to such a temperature (above 700°) that the changes which were suppressed when the steel was hardened by quenching are allowed to take place during the heating and cooling process.

In many metals the annealing process is liable to be complicated by the effects of chemical actions between the metal and its solid or gaseous surroundings, as well as by the effects of the growth of the constituent crystals of the metal; at high temperatures these crystals tend to increase in size, and the resulting coarsening of the grain of the metal leads to a deterioration in mechanical properties. Annealing at an unduly high temperature or for too long a time thus becomes 'over-heating,' and is injurious to almost all metals and alloys, notably to steel and brass. W. R.

ANODYNINE. Identical with antipyrine (*q.v.*).

ANONA MURICATA (Linn.). A decoction of the root is used as an antidote for fish-poisoning, and the bark serves as an astringent. The leaves are useful in softening abscesses, and from the seeds a wine can be prepared which is said to be beneficial in cases of diarrhœa (Chem. Zeit. 10, 433; J. Soc. Chem. Ind. 5, 332).

ANORTHITE *v.* FELSPAR.

ANOZOL. Trade name for a preparation of iodoform deodorised by 10–20 p.c. of thymol.

ANTHEMOL *v.* CAMPHORS.

ANTHIONE. Trade name for a solution of potassium persulphate. Employed as a photographic reagent.

ANTHOKIRRIN. The yellow crystalline matter of the flowers of the yellow toadflax (*Linaria vulgaris*). Formerly used as a dyeing material, but the colour is not permanent.

ANTHOKYAN. The expressed juice of the sweet or purple violet (*Viola odorata*), gently heated to 89°, then skimmed, cooled, and filtered. A little rectified spirit is then added, and the following day the whole is again filtered. Used to make syrup of violets, and to colour and flavour liqueurs.

ANTHOPHACIN. A term given by Möbius (Chem. Zentr. 1901, i. 190) to the brown colouring matter of flowers.

ANTHRACENE $C_{14}H_{10}$. Discovered by Dumas and Laurent in the highest boiling portion of coal tar, and termed by them *paranaphthalene* (Annalen, 5, 10); further examined by Laurent, who re-named it *anthracene* (Annalen, 34, 287); first obtained pure, and its composition determined, by Fritzsche (Annalen, 109, 249), and more exactly studied by Anderson (Annalen, 122, 294; Chem. Soc. Trans. 15, 44).

Occurrence.—Anthracene is one of the products of the destructive distillation of coal, and is found in the tar; the average yield of the pure hydrocarbon is about 0·3 p.c. of the tar obtained.

A new source of anthracene has been announced (Dingl. poly. J. 246, 429) in the tar obtained when the residue, left after the illuminating oils have been distilled from Baku petroleum, is allowed to fall on pumice in red-hot iron retorts. 1000 kilos of naphtha residue under these conditions yield 500 c.m. of gas, used to heat the retorts, and 300 kilos. of tar, containing about 0·2 p.c. of pure anthracene. The supply of the naphtha residue is, however, too limited to render anthracene from this source a serious competitor with that from coal tar.

According to Elliott (Amer. Chem. J. 6, 248), the tar obtained in the manufacture of gas by the destructive distillation of light petroleum naphtha boiling below 150° contains 2·63–2·90 p.c. of anthracene. A remarkable production of anthracene, during the distillation of the higher-boiling portions of crude phenol, has been observed by Köhler (Ber. 18, 859).

Anthracene is obtained by the distillation of rhein with zinc-dust (Oesterle and Tesza, Arch. Pharm. 1908, 432), but this production is of no commercial value.

Preparation (Auerbach, Das Anthracen und seine Derivate; Kopp, J. 1878, 1187; Perkin, Journ. Soc. Arts, 27, 572; Lunge, Coal Tar and Ammonia).—Anthracene is obtained from the 'green grease' which forms the last portion of the 'heavy oil' or 'dead oil' of the tar distiller; this at first is a brown liquid with a green fluorescence, but soon becomes semi-solid on standing, owing to the separation of solid substances. When no further separation occurs, the mass is subjected to filtration, either in a centrifugal machine or a filter press, first in the cold and finally at 40° (Gessert, Dingl. poly. J. 196, 543); or is filtered through strong linen bags, and afterwards submitted to hydraulic pressure in a press so arranged that the plates can be heated with steam and the cake hot-pressed. A notable quantity of anthracene remains dissolved in the expressed oil, and especially in the portions separated when the temperature is raised, and is recovered by redistilling and

working up the product as just described. The hard yellowish-green cake obtained, containing 25–40 p.c. of pure anthracene, is ground to a fine powder in mills and heated with coal-tar naphtha (b.p. 80°–100°), solvent naphtha (b.p. 120°–190°), creosote oil, or petroleum spirit (b.p. 70°–100°), in large iron vessels provided with stirrers. Petroleum spirit is to be preferred (Perkin), since it dissolves less anthracene whilst the impurities are sufficiently soluble in it to be removed if the quantity of solvent employed is 2–3 times as great as that of the anthracene to be purified. Solvent naphtha, consisting esentially of xylenes, pseudo-cumene and mesitylene, is extensively employed, as phenanthrene is much more soluble than anthracene in this solvent. When creosote oil is used, it must be free from naphthalene; the advantage of using creosote oil is that it dissolves out the methyl anthracene, the anthracene being practically insoluble therein. The residue contains from 45–50 p.c. of the hydrocarbon, but inasmuch as it is not readily reduced to powder, and unless finely divided is only slowly attacked by oxidising agents, it is sublimed by passing steam, heated at 220°–240°, over the melted product, and condensing the vapours in a chamber by jets of water. The anthracene thus obtained is in leafy masses, containing from 50–60 p.c. of the hydrocarbon, the chief impurities consisting of carbazole (10–12 p.c.), phenanthrene, pyrene, chrysene, and other hydrocarbons, together with small quantities of phenols of high boiling-point, and of acridine; it can readily be ground to a paste, and is now sufficiently pure for conversion into anthraquinone by oxidation. If, however, dichloranthracene is required, further purification is necessary; this can be effected by distillation with caustic potash, whereby impurities such as carbazole and bodies of a phenolic character are retained, and anthracene, together with phenanthrene, distils over with no greater loss than occurs if the 60 p.c. product is distilled alone; caustic soda cannot be substituted for the potash, since it produces no purification of any consequence. Instead of distilling washed anthracene (100 parts) with caustic potash, Perkin employs a mixture of Montreal potash (30 parts), which usually contains potassium hydroxide in considerable quantities, and caustic lime (6 parts). Unless lime is used, the residue in the retorts forms a hard cake, which can be removed only with difficulty. Hydrogen is evolved during the distillation. The distillate is freed from phenanthrene by washing with coal-tar naphtha, and the residue is a very pure anthracene. This production of phenanthrene, even from anthracene which has been freed from this impurity by extraction with solvents previous to distillation with caustic potash, is noteworthy and points to the probable existence of molecular compounds of phenanthrene with other of the impurities of the washed anthracene, which are destroyed during the distillation with caustic potash. This process of Perkin has been subjected to considerable criticism. According to Auerbach, a loss of anthracene to the extent of 10 p.c. occurs, and this, added to the cost of fuel employed, renders it the most costly method of purification yet devised. The great advantage of the method, however, is that it brings anthracenes of different origins to a similar condition of purity; even pitch anthracene—obtained by the distillation of gas-tar pitch in iron retorts with the aid of super-heated steam, and generally unsuitable for purification owing to the difficulty of removing higher hydrocarbons associated with it—works perfectly well after it has been subjected to this process.

Many modifications in the method of purifying crude anthracene have been introduced. A method based on the far greater solubility of the impurities in mixtures of aniline, pyridine, or quinoline bases, has been patented by the Chemische Fabriks-Actiengesellschaft in Hamburg (D. R. P. 42053 of April 15, 1887). The crude anthracene is dissolved at 100° in 1½–2 times its weight of a dehydrated and rectified mixture of tar bases (pyridines) separated from the light oil obtained in tar distillation (compare D. R. P. 34947 and 36372), and the solution, on cooling, yields a crystalline separation of anthracene almost free from carbazole and its homologues. The patentees state that a 33 p.c. anthracene dissolved in 1·75 times its weight of pyridine bases yields on crystallisation an 82·5 p.c. anthracene, whilst when dissolved in twice its weight of a mixture of equal parts of pyridine bases and benzene, it yields an 80 p.c. anthracene, and in twice its weight of a mixture of equal parts of benzene and aniline a 75 p.c. anthracene. The recovery of the anthracene contained in the mother liquors offers no special difficulty.

Remy and Erhart (D. R. P. 38417 of Jan. 19, 1886) have proposed crystallisation from oleic acid as a means of purification of crude anthracene. The difficulty of recovering the anthracene contained in the mother liquors would seem, however, to deprive this method of technical importance.

Graham (Chem. News, 33, 99, 168) has devised a method for recovering anthracene from the filtered oils used in its purification.

The Farbenfabriken vorm. Friedr. Baeyer & Co. (D. R. P. 68474; Eng. Pat. 5539; J. Soc. Chem. Ind. 1893, 439) employ liquid sulphur dioxide, which dissolves the impurities of crude anthracene, but very little anthracene itself. 600 kilos. crude anthracene is mixed in a wrought iron agitator with 2400 kilos. liquid sulphur dioxide, first exhausting the air and then allowing the sulphur dioxide to enter. The reaction having ceased, the mass is forced by its own vapour pressure into an iron steam-jacketed, filtering tower, where anthracene of 70–80 p.c. remains behind. The mother liquor is distilled, the sulphur dioxide being collected and recondensed by means of an air-compressor.

Another patent of the same firm (D. R. P. 78861; Eng. Pat. 7862; J. Soc. Chem. Ind. 1895, 361) recommends the use of acetone or other fatty ketones as a purifying agent. 560 kilos. crude anthracene is stirred in a steam-jacketed cylinder with 750 kilos. acetone for an hour. After cooling the separated anthracene is filtered and washed with 375 kilos. acetone. The second liquor is used over again, and the first is distilled to recover the acetone. From crude stuff containing 34 or 35 p.c. anthracene, an article of 82 p.c. is easily made, and only a few per cent. anthracene remain in the residue after distilling off the acetone. The acetone may be

used in the form of 'raw acetone' or 'acetone oils.'

Welton (Eng. Pat. 27559; D. R. P. 113291; J. Soc. Chem. Ind. 1900, 139) purifies crude anthracene by means of liquid (anhydrous) ammonia, which dissolves out most of the impurities, but not the anthracene itself.

Luyten and Blumer (Eng. Pat. 14892; D. R. P. 141186; J. Soc. Chem. Ind. 1901, 796) state that when anthracene is purified by solvents such as naphtha, acetone, &c., the presence of tar oil in the crude anthracene is beneficial. 25 parts of drained crude anthracene are heated with 35 parts of naphtha until the temperature is near that of the solvent. On cooling, the anthracene crystallises out and is filtered and washed with a little of the solvent. It is dried by heating to fusion, and distilling off the solvent; 80 p.c. anthracene is obtained by this method.

The Aktien Gesellschaft für Theer und Erdöl Industrie (D. R. P. 111359; Eng. Pat. 7868; J. Soc. Chem. Ind. 1899, 750) heat crude anthracene to fusion, and allow it to cool until 50 p.c. has crystallised, when the mother liquor is run off and again allowed to crystallise. The second crop can be raised to the value of the first (45–50 p.c.) by another fusion. This product is again fused and treated with caustic potash lye (50 p.c.) in quantity sufficient to react with the carbazole present. When the reaction is complete, the mass separates into two layers, the lower part being potassium carbazole. The upper anthracene layer is run into its own volume of 90's benzol, which dissolves any phenanthrene. The anthracene is pressed or centrifuged, and again washed with the same solvent, and is obtained as a pale-brown powder. By this means 30 p.c. anthracene is raised to 90 p.c. (*v.* also Scholvien, Fr. Pat. 335013; J. Soc. Chem. Ind. 1904, 113).

The Aktien Gesellschaft fur Anilinfabrik (D. R. P. 178764; J Soc. Chem. Ind. 1907, 1193) add potassium hydroxide to the melted crude anthracene, which is then distilled *in vacuô*, the anthracene distilling over being passed into some solvent in which it is soluble at the temperature of the reaction, and from which it crystallises on cooling. It is stated that 95–96 p.c. of the anthracene is recovered as a product containing 95–98 p.c. of pure anthracene.

Wirth (Eng. Pat. 14462; J. Soc. Chem. Ind. 1901, 464) separates the carbazole by means of its easily soluble nitroso- compound. Crude anthracene is mixed in a vessel provided with a stirrer with light coal-tar oil and sodium nitrite. Dilute sulphuric acid is added gradually, and the sodium sulphate which is formed is dissolved in water and separated from the light-oil layer. The anthracene is filtered from the light coal-tar oil, washed with benzene, and dried. It contains 75–95 p.c. anthracene, according to quality of the crude material.

Catchpole (Eng. Pat. 16641; D. R. P. 164508; J. Soc. Chem. Ind. 1903, 1190) places the crude product in the form of blocks or slabs on a perforated or channelled surface in a chamber suitably heated to a temperature not exceeding 200°, whereby the impurities are 'sweated' out. A slight washing with acid and distillation complete the process.

Vesely and Votocek (Eng. Pat. 27596; J. Soc. Chem. Ind. 1905, 191) find that concentrated sulphuric acid extracts the whole of the basic impurities of anthracene from a solution of crude anthracene in a solvent immiscible with sulphuric acid. The most suitable solvents are mineral and coal-tar oils, but carbon disulphide and chloroform may be used; 100 parts of crude anthracene (35 p.c.) are dissolved in 300 parts of solvent naphtha, 100 parts of concentrated sulphuric acid are added, and the mixture is heated and at the same time vigorously agitated for a few minutes. The sulphuric acid having been drawn off, the solution is freed from acid by agitation with calcium carbonate, filtered, and then allowed to crystallise. By this process it is stated to be possible to obtain an 85–90 p.c. anthracene, perfectly free from carbazole.

A troublesome impurity in anthracene is a peculiar paraffin, which has a high melting-point, and is only sparingly soluble either in light petroleum or coal-tar naphtha; it is dissolved to a certain extent by these solvents when hot, but on cooling is almost entirely deposited again. A small quantity left in the anthracene frequently impedes succeeding operations, and, owing to its stability, passes through most of the processes without change.

Syntheses.—From orthotolylketone, by heating with zinc-dust (Behr and Van Dorp, Ber. 7, 17); from orthobenzylbromide, by the action of sodium (Jackson and White, Ber. 12, 1965); from a mixture of benzene, acetylene tetrabromide, and aluminium chloride (Anschütz, Annalen, 235, 156); from benzene and aluminium chloride under the influence of nickel carbonyl at 100° (Dewar and Jones, Chem. Soc. Trans. 1904, 213); and by treating pentachlorethane in benzene with aluminium chloride, when anthracene is formed through the intermediate formation of perchlorethylene (Mouneyrat, Bull. Soc. chim. 19, [3] 557). An interesting synthesis resulting in the production of methyl anthracene (m.p. 200°) is that of Kraemer and Spilker (Ber. 1890, 3174). By the interaction of xylene and cinnamene, phenyltolylpentane is formed, which when passed through a red-hot tube forms methyl anthracene (m.p. 207°), hydrogen and methane being evolved. This synthetical production of methyl anthracene is of importance in its relation to the present theories of the mode of formation of anthracene in coal tar.

Properties.—Anthracene crystallises in glistening white scales. It melts at 216·5° (Reissert, Ber. 1890, 2245), and boils at 382° (Schweitzer, Annalen, 264, 193). When pure, it shows a bluish-violet fluorescence, but this is concealed if small quantities of yellow impurities (Fritzsche's chrysogen) are present. Yellow-coloured anthracene, on exposure to sunlight, is bleached, and becomes fluorescent, but under these conditions the hydrocarbon undergoes conversion into paranthracene $(C_{14}H_{10})_2$—a peculiar modification, which is much less soluble than anthracene, is unattacked by bromine and nitric acid at 100°, and does not combine with picric acid; it melts at 244°, and is thereby converted into ordinary anthracene (Fritzsche, J. pr. Chem. 101, 333; Graebe and Liebermann, Annalen, Suppl. 7, 264;

Schmidt, J. pr. Chem. [2] 9, 248). The fluorescence of anthracene and certain of its derivatives has been referred by Liebermann to a particular molecular grouping (Ber. 13, 913). Meyer (Zeitsch. physikal. Chem. 1897, 468) attributes fluorescence to the presence of what are known as fluorphoric groups, which must be situated between two heavy atomic groups, usually benzene nuclei. The solubility of anthracene in 100 parts of various solvents has been determined by Versmann (Jahresbericht. 1874, 423), Perkin (Journ. Soc. Arts, 27, 598: v. Becchi, Ber. 12, 1978), Findlay (Chem. Soc. Trans. 1902, 1221) with the following results :—

		Parts of anthracene
Alcohol (absolute)	at 16° dissolves	0·076 (B.).
,, ,,	b.p. ,,	0·830 (B.).
,, sp.gr. =0·800	at 15° ,,	0·591 (V.).
,, ,, =0·825	,, ,,	0·574 (V.).
,, ,, =0·830	,, ,,	0·491 (V.).
,, ,, =0·835	,, ,,	0·475 (V.).
,, ,, =0·840	,, ,,	0·460 (V.).
,, ,, =0·850	,, ,,	0·423 (V.).
Ether . .	,, ,,	1·175 (V.).
Chloroform .	,, ,,	1·736 (V.).
Carbon disulphide	,, ,,	1·478 (V.).
Acetic acid .	,, ,,	0·444 (V.).
Light petroleum .	,, ,,	0·394 (V.).
,, .	b.p. 70°–100° at 15° dissolves	0·115 (P.).
Benzene . .	,, ,,	1·296 (F.).
,, b.p. 80°–100°	,, ,,	0·976 (P.).
Toluene . .	at 16·5° ,,	0·920 (B.).
,, . .	at b.p. ,,	12·940 (B.).

When introduced into an alcoholic solution of picric acid saturated at 30°–40°, anthracene forms a picrate $C_{14}H_{10},C_6H_3(NO_2)_3O$, crystallising in glistening red needles which melt at 138°; it is decomposed into its constituents by alcohol, water, and dilute alkalis, even in the cold. The formation of the picrate is best obtained by warming molecular quantities of anthracene and picric acid on the water-bath in chloroform solution. On oxidation with potassium dichromate or manganese dioxide and sulphuric acid, anthracene is converted into anthraquinone, whilst strong nitric acid oxidises it to anthraquinone and dinitroanthraquinone; nitro- derivatives of anthracene can, however, be prepared by the action of strong nitric acid on the hydrocarbon, if care is taken to decompose any nitrous acid which may be formed during the reaction (Perkin, Chem. Soc. Proc. 1889, 13). Electrolytic oxidation in acetone yields anthraquinone (Fontana and Perkin, Chem. Zentr. 1904, ii. 708); the same product results by the electrolytic oxidation of a suspension of anthracene in a 2 p.c. solution of cerium sulphate in 20 p.c. sulphuric acid at 80°–90° (Farb. vorm. Meister, Lucius and Bruning, D. R. P. 152063; Chem. Zentr. 1904, ii. 71); or by the oxidation of anthracene by cerium oxide in sulphuric acid (Farb. M. L. & B.; D. R. P. 158609; Chem. Zentr. 1905, i. 840); or by heating anthracene with charcoal at 150°–300° (Dennstedt and Hassler, D. R. P. 203848; Chem. Zentr. 1908, ii. 1750).

Concentrated sulphuric acid converts anthracene into sulphonic acids. Anthracene monosulphonic acid is obtained by the direct sulphonation of anthracene with sulphuric acid of 53° or 54°B., and about 60 p.c. of the anthracene employed is thus converted. If sulphuric acid of 66°B. is used, two isomeric disulphonic acids are obtained, and these, on oxidation, yield two anthraquinonedisulphonic acids, which are isomeric with the two acids obtained by the direct sulphonation of anthraquinone. The β-anthracene disulphonic acid, after oxidation with chromic or nitric acids, and subsequent fusion with alkali, yields *alizarin* (*q.v.*), and the monosulphonic acid similarly treated yields *anthrapurpurin* (*q.v.*) (La Société Anonomye des Matières Colorantes et Produits Chemiques de St. Denis, Eng. Pat. 1280; J. Soc. Chem. Ind. 1894, 32).

The same acids are obtained by heating anthracene with alkali bisulphate to 140°–150° (D. R. P. 77311). Anthracene is readily attacked by chlorine and bromine, and yields with each element a series of additive and substitution derivatives; additive compounds, apparently, are the first products of the action, and these either decompose during the reaction or can be decomposed by boiling with alcoholic potash into the corresponding substitution derivatives, which also form additive compounds by the further action of the halogens. The chloranthracenes are now prepared on a large scale (Clayton Aniline Co., Eng. Pat. 8744; J. Soc. Chem. Ind. 1906, 64). Dry chlorine reacts with anthracene in the presence of lead peroxide at a high temperature. Fifty parts by weight of anthracene and 10 parts of dry powdered lead peroxide are treated with dry chlorine at 220° until the weight has increased to 120 parts. The temperature, however, may be varied between 180° and 260°, and the composition of the product varies with the temperature employed and the amount of chlorine absorbed. The product consists mainly of β-tetrachloranthracene (m.p. 152°), which is readily soluble in benzene and crystallises out in yellow needles, and another part much less soluble in benzene and more highly chlorinated. This latter consists of two products: hexachloranthracene (m.p. 277°), which crystallises from nitrobenzene, and heptachloranthracene (m.p. 232°), which is more soluble in benzene than the former. Oxidation converts these compounds into chloranthraquinones, containing 2 atoms of chlorine less than the original compound. Treatment with a mixture of nitric and sulphuric acids results in the formation of chlornitroanthraquinones which yield dyestuffs on treatment with fuming sulphuric acid. The chloranthraquinones on treatment with fuming sulphuric acid in the presence or absence of boric acid, yield hydroxy- compounds; *e.g.* 1 : 4 dichloranthraquinone yields *quinizarin* (*q.v.*) (Farb. vorm. F. Baeyer & Co., Fr. Pat. 385358; J. Soc. Chem. Ind. 1908, 557). Reducing agents, such as sodium amalgam or phosphorus and hydrogen iodide, convert anthracene into the dihydride (Graebe and Liebermann, *l.c.*; Liebermann and Topf., Annalen, 212, 5); hydrogen and nickel oxide at 260°–270° and 100–125 atmos. convert anthracene first into tetrahydro-, then decahydro-, and finally perhydroanthracene (Ipatieff, Jokowleff, and Rakitin, Ber. 1908, 996).

Estimation.—Luck (Ber. 6, 1347); Meister, Lucius, and Bruning (Dingl. poly. J. 224, 559); Nicol (Chem. Soc. Trans. 1876, 2, 553); Bassett

(Chem. News, 73, 178; 79, 157). The percentage of anthracene in a sample of the commercial product is determined by oxidising it to anthraquinone with chromic acid, dissolving the product in sulphuric acid, and precipitating with water, since the associated impurities are either destroyed during the oxidation or are converted into sulphonic acids soluble in water. The details of the process are as follows: 1 gram of anthracene is introduced with 45 c.c. of acetic acid into a flask connected with a reversed condenser, and heated to boiling; a solution of 15 grams of chromic acid in 10 c.c. of acetic acid and 10 c.c. of water is then added, drop by drop, to the boiling solution during a period of 2 hours; and the product is boiled for 2 hours longer, allowed to stand for 12 hours, then poured into 400 c.c. of water, and, after standing for 3 hours longer, is filtered. The anthraquinone on the filter is washed with water, with hot dilute alkali, and then with hot water; afterwards it is placed in a small dish dried at 100°, and digested for 10 minutes with 10 times its weight of pure concentrated sulphuric acid at 100°. The solution of anthraquinone is sulphuric acid is then allowed to remain for 19 hours in a moist atmosphere, mixed with 200 c.c. of water, and the precipitated anthraquinone filtered off and washed first with water, then with dilute alkali, and finally with water; it is then dried at 100° in a dish, weighed, ignited, and the ash deducted from the first weighing. The difference gives the weight of anthraquinone corresponding to the amount of anthracene present in the sample.

Impurities.—Paraffin is usually present in crude anthracene, and is estimated by treating the material with fuming nitric acid, keeping the mass cold. When all the acid has been added, the mixture is kept at the ordinary temperature until the anthracene has dissolved, and then heated until the paraffin has melted. The solution is filtered and the precipitate washed with fuming nitric acid until the filtrate dissolves in water without turbidity, and then with water until neutral. Finally, the paraffin is washed with alcohol, dissolved in warm ether and the filtrates collected in a weighed porcelain dish; the filtrates are evaporated and the paraffin dried at 105°–110° for half an hour (Heusler and Herde, J. Soc. Chem. Ind. 1895, 828). The detection of carbazole and phenanthrene in the purified product is carried out as follows:—

Carbazole. Sample is extracted in cold with ethyl acetate, solution allowed to evaporate, and residue transferred by a few drops of same solvent to a watch-glass. On evaporation, carbazole is left behind; when treated with a drop of nitrobenzene and phenanthraquinone, it yields characteristic small copper coloured plates.

Phenanthrene. Sample is extracted with benzene, and the evaporation residue treated with *α*-dinitrophenanthraquinone in nitrobenzene. In this case mixed crystals are obtained having the form and colour of the brown needles of the phenanthrene compound, but containing a large quantity of anthracene.

ANTHRACENE ACID BROWN, -CHROME BLACK, -RED, -YELLOW *v.* AZO- COLOURING MATTERS.

ANTHRACENE GREEN. *Cœrulein* and *Cœrulein S.* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS; also XANTHINE COLOURING MATTERS).

ANTHRACENE VIOLET. *Gallein* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS; also XANTHINE COLOURING MATTERS).

ANTHRACHRYSONE *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRACITE *v.* FUEL.

ANTHRACITE BLACK *v.* AZO- COLOURING MATTERS.

ANTHRACOXENE *v.* RESINS.

ANTHRACYL CHROME GREEN *v.* AZO- COLOURING MATTERS.

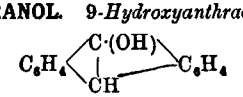
ANTHRAFLAVIC ACID *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAGALLOL *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAGALLOL DIMETHYL ETHERS *v.* CHAY ROOT.

ANTHRANIL, ANTHRANILIC ACID (*o-aminobenzoic acid*) *v.* AMINOBENZOIC ACID AND HOMOLOGUES.

ANTHRANOL. *9-Hydroxyanthracene*



is prepared by the reduction of anthraquinone with hydriodic acid and phosphorus (Liebermann and Topf, Annalen, 212, 6; Ber. 1876, 1201), or with tin and acetic acid (Liebermann and Gimbel, Ber. 1887, 1854). Another method is to add copper or aluminium powder to anthraquinone dissolved in concentrated sulphuric acid at 30°–40°, and pour the product into water. The crude substance is recrystallised from glacial acetic acid containing a trace of aluminium and a little hydrochloric acid (Baeyer & Co., D. R. P. 201542; Chem. Zentr. 1908, ii. 1218; Bezdzik and Friedlander, Monatsh. 30, 871). Anthranol has been synthesised by heating 1 part of *o*-benzylbenzoic acid with 2 parts of sulphuric acid at 100° (Fischer and Schmidt, Ber. 1894, 2789). It crystallises in colourless needles, m.p. 165°, with decomposition. It dissolves in alkalis, and then behaves as its tautomeride anthrol (*q.v.*); *e.g.* it condenses with benzaldehyde to form benzilidine anthrol (Haller and Padova, Compt. rend. 141, 857, *v.* also Bad. Anil. und Soda Fab., D. R. P. 172930; Chem. Zentr. 1906, ii. 834). By heating the alkaline solution of anthranol for some time, it becomes oxidised to anthraquinone; hydroxylamine hydrochloride converts it into anthraquinonedioxime (Nietzki and Kehrmann, Ber. 1887, 613). Anthranol yields a benzoyl derivative (m.p. 164°) with benzoyl chloride in pyridine (Padova, Compt. rend. 143, 121; Ann. Chim. Phys. [8] 19, 353), and a diiodide with iodine in benzene solution (Liebermann, Glawe and Lindenbaum, Ber. 1904, 3337).

Dianthranol $C_{28}H_{18}O_2$ is formed, together with a little anthraquinone, when anthranol dissolved in benzene is exposed to sunlight for some weeks, or when the benzene solution is boiled for some hours. Colourless tabular crystals (m.p. 250°) (Orndorff and Bliss, Amer. Chem. J. 1896, 453; Orndorff and Cameron, Amer. Chem. J. 1895, 658).

ANTHRAPURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAQUINONE $C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4$.

Obtained by the oxidation of anthracene with chromic acid (Kopp, Jahresbericht. 1878, 1188; Laurent, Ann. Chim. Phys. [2] 60, 220; 72, 415; Annalen, 34, 287; Anderson, Annalen, 122, 301; Graebe and Liebermann, Annalen, Spl. 7, 285); by the distillation of calcium benzoate (Kekulé and Franchimont, Ber. 1872, 908); by the distillation of benzoic acid with phosphorus pentoxide; by the distillation of *o*-benzoylbenzoic acid with phosphorus pentoxide, or by heating it alone (Ullmann, Annalen, 291, 24; Behr and Dorp, Ber. 1874, 578; Liebermann, Ber. 1874, 805; Perkin, Chem. Soc. Trans. 1891, 1012); by the dry distillation of calcium phthalate (Panaotovits, Ber. 1884, 13). Heller (Zeitsch. angew. Chem. 1906, 19, 669) heats 1 part of phthalic anhydride with 3·5 parts of benzene and 1·8 parts of aluminium chloride in a lead vessel at 70° until the evolution of hydrogen chloride ceases. After cooling, water is added and the excess of benzene removed by steam distillation. The solution is made alkaline and boiled, and then on addition of acid benzoyl benzoic acid is precipitated. On heating this for one hour at 150°, anthraquinone is obtained (*cf.* Piccard, Ber. 1874, 1785; Friedel and Crafts, Ann. Chim. Phys. [6] 1, 523; Müller, J. 1863, 393). Phenyl-*o*-tolylketone gives anthraquinone on heating with lead oxide or on oxidation with manganese dioxide and sulphuric acid (Behr and Dorp, Ber. 1873, 754; 1874, 16; Thörner and Zincke, Ber. 1877, 1479).

Industrial preparation.—Crude anthracene (55–60 p.c.) is slowly added to a hot solution of potassium dichromate in a large wood vat lined with lead. The solution is kept well stirred and heated with steam until all the anthracene has been added. The steam is then cut off and sulphuric acid is run into the mixture in the form of a fine spray; the heat generated by the reaction keeps the solution boiling. The crude anthraquinone is then separated by filtration and dried. It is dissolved in sulphuric acid without applying any heat, and, when solution is complete, transferred to a large vat lined with lead and boiled with water. The precipitated anthraquinone is at once separated by means of filter presses from the soluble compounds; the pressed cakes are boiled with a solution of soda, and then again filtered, pressed, dried, and finally sublimed (Levinstein, J. Soc. Chem. Ind. 1883, 219; Kopp. *l.c.*). Poirrier and Rosenstiehl (Eng. Pat. 8431; J. Soc. Chem. Ind. 1887, 595) oxidise anthracene in a closed lead-lined vessel by means of ferric sulphate. The vessel is heated to 120°–150° during 72 hours, compressed air being injected into the vessel. By this means the anthracene is virtually oxidised by the air, the ferric sulphate acting as a carrier for oxygen. Another process consists in the absorption of nitric oxides diluted with air, by zinc oxide, copper oxide, or a similar oxide of low basicity. Anthracene is mixed with this, and a stream of air or oxygen is passed through the mixture at 250°–350°, anthraquinone being produced (Ch. Fabr. Grünau, Landshoff & Meyer, D. R. P. 207170, 215335; J. Soc. Chem. Ind. 1909, 360, 1310). Darmstädter (Chem. Zentr. 1900, ii, 151; D. R. P. 109012) prepares anthraquinone by the electrolytic oxidation of anthracene in a chromic-acid bath. Various processes have been patented for purifying the crude anthraquinone thus produced. Bronner (J. Soc. Chem. Ind. 1882, 499; 1883, 410; Eng. Pat. 759; D. R. P. 21681) dissolves out the impurities on a specially constructed circular shelf. The method depends on the continuous extraction of the impure product with an amount of solvent insufficient to keep in solution the whole of the anthraquinone and the easily soluble impurities. Bayer & Co. (D. R. P. 68474; Eng. Pat. 5539; J. Soc. Chem. Ind. 1893, 439) dissolve out the impurities with liquid sulphur dioxide; Sadler & Co. Ltd. and Driedger (Eng. Pat. 17635; J. Soc. Chem. Ind. 1902, 1072) recrystallise the crude anthraquinone from hot aniline.

Properties.—Anthraquinone, as usually prepared, forms a felted mass of crystals of a pale-yellow or buff colour; by sublimation it can be obtained in the form of lemon-yellow needles or golden-yellow prisms; m.p. 277°; b.p. 379°–381° (corr.) (Recklinghausen, Ber. 1893, 1515); sp.gr. 1·438–1·419 (Schroeder, *ibid.* 1880, 1071). Sparingly soluble in alcohol and ether, somewhat more soluble in hot benzene. It is neutral in its reactions, and is insoluble in dilute acids or alkalis. Anthraquinone is very stable; it is not affected by hot hydrochloric acid, or by boiling with caustic potash or calcium hydroxide solutions; it dissolves in hot nitric acid (sp.gr. 1·4), and is deposited in crystals on cooling or on dilution; it dissolves unchanged in concentrated sulphuric acid at 100°, and is precipitated in fine crystals on pouring into water. Strongly heated with sulphuric acid, it is converted into mono- and di-sulphonic acids (*v.* ALIZARIN). Anthraquinone is of great commercial importance, as it is used in the preparation of alizarin, quinizarin, purpurin, &c. (*v.* ALIZARIN). Fusion with zinc or treatment with sodium methoxide converts it into anthracene (Haller and Minguin, Compt. rend. 120, 1105); fusion with caustic soda converts it into sodium benzoate (Graebe and Liebermann, Annalen, 160, 129), and by distilling it over lime benzene is formed; reduction with zinc and caustic soda, or with sodium amalgam yields oxanthranol $C_{14}H_{10}O_2$ and dianthranol (Diels and Rhodius, Ber. 1909, 1076; Meyer, Ber. 1909, 143); zinc and amyl alcohol converts it into dianthrol (Meyer, Monatsh. 30, 165). Phosphorus pentachloride and phosphorus oxychloride convert it into trichloranthracene and other chlorinated products (Radulescu, Chem. Zentr. 1908, ii. 1032). A delicate test for anthraquinone consists in reducing it with sodium amalgam in dry ether. On adding a drop of water, a red colouration is produced; if alcohol is used instead of ether, addition of water gives a green colouration (Claus, Ber. 1877, 927).

Condensation products.—With phenols: Scharwin and Kusnezof, Ber. 1903, 2020; 1904, 3616; Deichler, D. R. P. 109344; Chem. Zentr. 1900, ii. 360. With amines: Bayer & Co. D. R. P. 86150, 107730, 136777, 136788, 148079; Chem. Zentr. 1902, ii. 1272; Chem. Soc. Abst. 1904, i. 326. Aryl ethers, aryl- and alkyl-amino- derivatives: Bayer & Co. D. R. P.

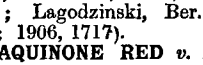
158531; Fr. Pat. 354717, 362140; J. Soc. Chem. Ind. 1905, 885, 1105; 1906, 752. Thiocyanates: Bayer & Co. D. R. P. 206054; J. Soc. Chem. Ind. 1909, 239. Mercaptans: *ibid.* 469.

1.2- and 1.4-anthraquinones have been prepared from α-anthrol and 1.2 -anthraquinone from β-anthrol (*v.* Dienel, Ber. 1906, 926; Liebermann, Ber. 1906, 2089; Harlinger, Ber. 1906, 3537; Lagodzinski, Ber. 1894, 1483; 1895, 1422; 1906, 1717).

ANTHRAQUINONE RED *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRARUFIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHROL



Two isomeric anthrols are known, α- or 1-hydroxyanthracene and β- or 2-hydroxyanthracene.

α-Anthrol is prepared by fusing 1-anthracenesulphonic acid with 5 parts of caustic potash at 250°, dissolving the mass in water, and filtering off the yellow flocks which separate out. The crude product is recrystallised from acetic acid and water. It forms yellow plates, m.p. 152°. α-Anthrol dissolves in the ordinary solvents with a blue fluorescence, and is more soluble than β-anthrol (Schmidt, Ber. 1904, 66; Dienel, Ber. 1905, 2862; *v.* also Linke, J. pr. Chem. [2] 11, 227).

-Anthrol is prepared by fusing 2-anthracenesulphonic acid with potash and recrystallising the crude product from acetone (Liebermann and Hörmann, Ber. 1879, 589; Linke, J. pr. Chem. [2] 11, 222). It can also be obtained by reducing hydroxyanthraquinone with hydriodic acid and phosphorus (Liebermann and Simon, Ber. 1881, 123). It forms yellow plates melting with decomposition at 200°, and is soluble in the common organic solvents with a violet fluorescence. By reduction with sodium in alcoholic solution, dihydroanthrol is obtained (Bamberger and Hoffmann, Ber. 1893, 3069), and by heating with acetamide at 280° *anthramin* is obtained. Azo-dyestuffs have been obtained from β-anthrol (Act. Ges. f. Anilinf. D. R. P. 21178; Frdl. i. 538).

ANTIAR RESIN or **UPAS ANTIAR.** A green resin which exudes from the upas tree (*Antiaris toxicaria* (Lesch.), order Maraceæ). Light petroleum and benzene extract from it a substance analogous to caoutchouc, a fatty matter, and two resinous substances; alcohol extracts from the residue a very poisonous glucoside, *antiarin* (De Vrij and Ludwig, J. pr. Chem. 103, 253).

ANTIARIN *v.* GLUCOSIDES.

ANTI-CHLOR. Linen and cotton fibres and paper pulp are apt to retain some free chlorine from the hypochlorite used in bleaching, and as this causes the material to rot slowly, the manufacturers use certain reagents known as 'anti-chlors' to remove the last traces of chlorine. The first substances employed were the neutral and acid sulphites of soda (sodium sulphite and bisulphite); these were superseded in 1853 by sodium hyposulphite, which is now very largely employed. Calcium sulphide, made by boiling milk of lime with sulphur; stannous chloride in hydrochloric acid with subsequent treatment with sodium carbonate to neutralise any free acid; ammonia, and sodium nitrite have also been recommended.

ANTIDIABETINE. Trade name for a preparation said to be composed of saccharin and mannite.

ANTI-FEBRIN. A trade name for *acetanilide* or *phenylacetamide* $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$. Discovered by Gerhardt in 1853, and investigated as an antipyretic by Kussmaul in 1886 (*v.* ACETANILIDE).

ANTIFORMIN. Trade name for the alkaline liquid prepared by adding caustic soda to a solution of sodium hypochlorite. Used as a disinfectant, the active ingredient being the chlorine, of which 4 p.c. is liberated on treatment with hydrochloric acid. Solutions of sodium hypochlorite are prepared in Germany by the electrolysis of 5 p.c. salt solution. A current of 110 volts and 100 amperes furnishes nearly 6000 litres daily of a disinfecting or bleaching solution containing 1 p.c. of available chlorine.

According to H. Will (Zeitsch. Ges. Brauw. 1903, 865; J. Soc. Chem. Ind. 1904, 125), it is one of the best disinfectants for brewery work. It rapidly softens organic impurities and facilitates their removal by scouring, in addition to its oxidising action, and it also dissolves incrustation. Its germicidal power is high, and a 5 p.c. solution is sufficient for most purposes. It is used cold, and may be safely applied to varnished surfaces with a brush, provided care is taken to prevent prolonged contact.

ANTIFUNGIN. Trade name for magnesium borate, employed as a fungicide.

ANTIGERMIN. Trade name for a preparation of a copper salt of a weak organic acid, mixed with lime. It is used as a fungicide.

ANTIHYPO. A solution of potassium percarbonate, used for destroying sodium thiosulphate in photographic negatives and prints.

ANTIMONIN. Trade name for antimony calcium lactate, used as a tannin-fixing mordant.

ANTIMONITE. Native antimony sulphide (*v.* ANTIMONY).

ANTIMONY. (*Antimoine*, Fr.; *Antimon*, Ger.) *Stibium.* Sym. Sb. At. wt. 120·2.

Occurrence.—Antimony occurs native in small quantities, occasionally in rhombohedral crystals, at Andreasberg in the Hartz, Przibram in Bohemia, Sala in Sweden, Allemont in France, in the United States, New South Wales, and Quebec. It occurs in large masses in Sarawak, Borneo.

Combined with *oxygen* as the sesquioxide Sb_2O_3, it occurs in *antimony bloom*, *white antimony*, or *valentinite*, and in *senarmontite*, being found in workable quantities in the Algerian province of Constantine. In *antimony ochre* or *cervantite*, and in *stibiconite* and *volgerite*, it occurs as antimonite of antimony Sb_2O_4.

Combined with *sulphur*, it occurs as *stibnite*, *antimonite*, or *grey antimony ore* Sb_2S_3. In union with *sulphur* and *oxygen* together, it forms *red antimony*, *antimony blende* or *kermesite* $Sb_2O_3 2Sb_2S_3$.

With *arsenic*, antimony is found in *allemontite* or *arsenical antimony*. With *silver*, in *discrasite*.

With sulphur and metals, antimony forms a number of *sulphantimonites*, among which may be mentioned *zinkenite*, *jamesonite*, *boulangerite*,

and *feather ore*, containing antimony, sulphur, and lead; *miargyrite*, *pyrargyrite*, and *stephanite*, containing silver; *berthierite*, containing iron, and *antimonial copper glance*. Antimony is found in certain ferruginous waters.

The antimony minerals of commercial importance as ores are *stibnite*, and the decomposition products which are usually associated with it and sometimes entirely replace it, viz. *kermesite*, *valentinite*, *senarmontite*, and *cervantite*.

Antimony ores occur in workable quantities in Mexico, California, North America, Canada, Australia, Japan, Borneo, Cape of Good Hope, New Zealand, Asia Minor, Algiers, Italy, Spain, Portugal, Corsica, and Sardinia. Small deposits of antimony sulphide have been discovered in Cornwall, Cumberland, and Scotland.

The veins in which stibnite is found are usually 4–6 inches in width, but in some rich mines, as in Nevada, they are several feet across. The gangue materials are quartz, with some brown-spar and heavy spar, and from these the sulphide can only be separated by hand-picking or liquation. It is occasionally found in pockets, when it is usually very pure.

By far the most general ore of antimony is the sulphide, but in some cases, as in Algeria, the oxide is found in workable quantities, and in other cases both oxide and sulphide occur together.

Extraction.—Metallic antimony and its compounds are nearly always extracted from the ores by dry methods. According to their suitability for the several methods of treatment, the ores fall into two broad classes:

(*a*) Sulphide ores containing over 40 p.c. stibnite.

(*b*) Sulphide ores containing less than 40 p.c. of the sulphide, and oxide ores of any grade. In this class also may be included liquation residues and flue deposits, &c.

Preliminary treatment of ores.—Ores of class (*a*) are used for the production of the metal by the English process. If the content of sulphide is over 90 p.c., the ore requires no preliminary treatment, but less pure ore is subjected to a process of *liquation*, in which the sulphide is melted and allowed to run away from the gangue.

The following method of liquation was formerly used where fuel is plentiful, as at Malbosc, in the Department of Ardèche, Wolfsberg in the Hartz, and in Hungary. The ore was placed in small lumps in a number of conical pots of 45 kilos. capacity, each perforated below and standing on a perforated plate over a sunken receiver. The pots were surrounded by fuel which continued to burn for 10 hours, the melted sulphide collecting in the receivers.

At La Lincouln, Wolfsberg, and Haute Loire, the pots were contained in a reverberatory furnace. At Schmöllnitz, in Hungary, the melted sulphide ran through channels into receivers outside the furnace.

At Malbosc, the pots are replaced by cylindrical tubes, perforated below and standing on similarly perforated plates above the receivers. Each cylinder has a capacity of 500 lbs. of ore, four being heated in one furnace. Each has a hole at the side, through which the residues are removed, these holes being closed during the heating. The receivers are of clay, or of iron coated with clay.

The method of liquation in reverberatory furnaces is used in some places where ore can be mined cheaply but fuel is dear. The consumption of fuel per unit of sulphide liquated is least with this type of furnace, but there is a considerable loss of antimony by volatilisation. This loss, however, can be prevented by the use of suitable condensing apparatus such as Herrenschmidt's (*v.i.*).

In any process of liquation the temperature must be carefully regulated, as too low a temperature results in a low yield of sulphide, the residues containing too much antimony, while too high a temperature increases the loss by volatilisation.

Ores of class (*b*) are either roasted to the non-volatile tetroxide, or to the volatile trioxide, or are subjected to one of the direct reduction processes.

The oxidation of the sulphide to tetroxide takes place at temperatures between 350° and 400° in presence of excess of air. If the ore is impure, antimonates of the metallic impurities are formed at the same time. During the roasting there is a great tendency for the ore to frit, and this necessitates the constant rabbling of the charge. The presence of gangue renders the ore less liable to fuse, so that the process is most easily carried out with poor ores, *e.g.* ore-dust, for the treatment of which it is largely used. The furnaces employed are of two classes:

(*a*) Rabble furnaces, having an egg-shaped flat bed, with a furnace on either side and a working door at the front. With these the process is intermittent.

(*b*) "Fortschaufelungsofen," in which the roasting is carried on continuously. These furnaces are 40–45 feet long, by 8 feet high, by 2 feet wide, and have 10 working doors on each side. The ore is charged in at one end, and is then gradually worked along the bed during about 40 hours, and finally discharged at the other end. Fresh ore is continually charged into the furnace at the rate of 6 cwts. every 8 hours.

The oxidation of the sulphide to volatile trioxide takes place at about 400° with a carefully regulated amount of air. This process, provided suitable condensation apparatus is installed, presents marked advantages, and is finding an increasing application, especially in dealing with poor ores. It may be noted that arsenic is completely separated as the more volatile trioxide, that any gold or silver present is left in the residues and can afterwards be extracted, that there is no loss of antimony, and that the consumption of fuel is low. Many different forms of plant have been used for this process, but in most the roasting takes place in a cupola or reverberatory furnace. The earlier forms of condensing apparatus are of two classes:

(*a*) In which the vapours are passed through a series of flues and chambers and finally through water-tanks in which the last traces of oxide are deposited.

(*b*) In which the furnace gases are cooled below 100° in flues and then filtered through canvas or other coarse fabric (*v.* Chatillon, Fr. Pat. 189974, 1888; and 382504, 1907; Woolford, Fr. Pat. 200245, 1889; Plews, U.S. Pat. 704367, 1902). Herrenschmidt has patented a complete plant for this process (Fr. Pat. 333306,

1903, and 386107, 1908), which differs materially from any earlier apparatus.

The roasting furnace is partly of brick and partly cast metal, and is provided with a hopper through which the ore, mixed with 4–5 p.c. of gas-coke or 6–7 p.c. charcoal, is introduced. The gases pass from the furnace into a chamber, and then through a series of cast-iron tubes placed nearly vertical and air-cooled, in which the main portion of the trioxide is deposited. The last traces are removed by forcing the gases up a tower filled with coke over which water flows. The draught is maintained by two centrifugal fans, working tandem. It is stated that 6 tons of ore, containing 10–15 p.c. antimony, can be treated in 24 hours, with a yield of over 90 p.c., and that the cost of producing 1 ton of oxide is 70 francs.

Smelting of the metal.—Antimony is prepared from 'crude antimony' or high-grade stibnite ores by the 'English' or 'precipitation' method. The ore, of which the composition has been determined by analysis, is ground under edge-runners to the size of a hazel-nut, or smaller, and is subjected to three operations:

Singling. This process is carried out in crucibles of which about forty are arranged in a double row on the hearth of a long reverberatory furnace having a grate at each end, and a flue, leading to condensing chambers, in the middle. The crucibles are about 20 inches high and 11 inches across, and are made of a mixture of 6 parts fire-clay and 1 part plumbago. The charge for each pot is 42 lbs. ore, 16 lbs. iron (of which about 2 lbs. is in the form of turnings, and 14 lbs. as tin-plate cuttings beaten into a ball), 4 lbs. salt, and 1 lb. slag from 'doubling' (*v.i.*). These materials are introduced into the red-hot crucible, and kept in a state of fusion for 2–3 hours, at the end of which time the contents are poured into moulds, and the antimony is removed from beneath the slag. The product, known as *singles*, usually contains about 91 p.c. antimony.

Doubling is carried out in crucibles arranged in a furnace as previously described. The charge for each pot is 84 lbs. broken singles, 7–8 lbs. liquated sulphide, and 4 lbs. salt, and the fusion, which takes about 1½ hours, is closely watched, the workmen judging from the nature of the slag when the operation is complete. The slag is then removed with an iron ladle, and the metal run into moulds. This product is called *bowl metal* or *star bowls*.

Frenching, or *melting for star metal* (*v.i.* under *Refining*).

In the English process the loss due to slagging and volatilisation is small, being only 2–5 p.c.

The sulphide may be mixed with half its weight of charcoal to prevent caking, and roasted at a gentle heat, the heat being gradually increased, but not to melting, whereby large quantities of sulphurous acid, arsenious oxide and antimonious oxide are evolved, the two latter being collected in flues. 20 p.c. of the antimony is stated to pass off in this operation, the greyish or red mass which remains consisting of antimony tetroxide containing about one-sixth of its weight of the trioxide and some sulphide. This residue, known as antimony ash, is mixed with 0·5 part of cream of tartar, or 1 part charcoal and 0·5 part of potash, or ½ part charcoal saturated with a concentrated solution of sodium carbonate, and fused in a covered crucible at a low red heat, and poured into a hot mould. 100 parts of sulphide yield 44 parts of antimony. The slag which rises above the metal consists of alkaline carbonate mixed with double sulphide of antimony and potassium or sodium with charcoal, and is known as *crocus of antimony*. The action of the charcoal in this reduction consists in the removal of the oxygen from the antimony oxide, producing metallic antimony, and in the reduction of a part of the alkali. The alkaline metal thus set free combines with the sulphur of a part of the antimonious sulphide, freeing an equivalent quantity of the antimony and forming a double sulphide of antimony and potassium with a further quantity of the sulphide.

The sulphide may also be reduced by fusing 8 parts of sulphide with 6 parts of cream of tartar in a crucible heated nearly to redness, then adding 2 or 3 parts of potassium nitrate, and fusing until perfectly liquid; or 8 parts of sulphide are mixed with 6 parts of cream of tartar and 3 parts of nitre, and are thrown in portions into a red-hot crucible and heated until perfectly fluid. By quietly fusing, with frequent stirring to prevent frothing, a mixture of 8 parts sulphide, 1 part sodium carbonate, and 1 part charcoal, 66 p.c. of metal is said to be obtained from the sulphide.

It is possible also to reduce the sulphide on the hearth of a reverberatory furnace. The partially roasted ore, which contains the sulphide and oxides of antimony, is mixed and fused with 8–13 p.c. of coal and 9–11 p.c. of soda, frequently with the addition of iron, in which case the slag produced is much less fusible and does not entirely cover the bath of metal; the antimony produced also contains much iron (Dingl. poly. J. 162, 449). Where carbonate of soda is used for the fusion the mass froths considerably and attacks the furnace hearth.

The metal is prepared from either of the oxides by one of the numerous reduction processes now in use.

(*a*) Reduction in reverberatory furnaces is carried out at Bouc, Septèmes, New Brunswick, &c. The furnace-bed is egg-shaped, deep in proportion to its width, and is provided with a tap-hole at the lowest point. The furnace gases are passed through a long series of condensing chambers. First 90–110 lbs. flux (chiefly salt, with some soda and sodium sulphate) and 220–230 lbs. of slag from a previous operation are melted on the hearth, and then 400–500 lbs. of roasted ore and 67–75 lbs. of charcoal are added, and the whole kept in a state of fusion till reduction is complete. At New Brunswick the reduction and refining are carried out consecutively in the same operation.

(*b*) Some French smelters reduce an oxidised ore containing 30–40 p.c. of antimony in a 3-tuyered shaft furnace at the rate of 2–2½ tons per 24 hours, with the consumption of about half that weight of coke. The regulus contains 92–95 p.c. of antimony, and is subsequently refined.

At Bánya, Hungary, antimony ores are mixed with silicious material and smelted in a blast-furnace for impure regulus, which is then

refined in a reverberatory furnace. The blast-furnace used is a round stack 6 m. high and 1·4 m. diameter at the throat. The hearth, which is 1 m. across, is fitted with five water-jacketed tuyeres, and has two outlets for slag and metal respectively; a third opening is used for blowing out. A blast of 15 c.m. per minute is used, and the gases are collected by a tube at the throat and passed through a condensing apparatus. Such a furnace will run for 3 weeks continuously, smelting about 20 tons of material daily (Berg. u. Hütt. Zeit. 1886, p. 102).

(c) Reduction in crucibles is only used when rich ore or the trioxide is available. The reducing agent is carbon (charcoal or anthracite), and sodium sulphate and carbonate are added to form a slag.

Considerable quantities of antimony ore are now treated directly for the production of the metal. One such process which has been successfully used for some time depends on the reduction of the sulphide in a bath of molten ferrous sulphide containing iron (*v.* T. C. Sanderson, U.S. Pat. 714040, 1902; Cookson, Fr. Pat. 324864 1902; and Herrenschmidt, Fr. Pat. 296200, 1900).

Another method consists in the reduction of the sulphide with carbon in water-jacketed blast-furnaces. This has been used by Hering for the treatment of liquation residues.

Germot (Revue des Produits Chemiques, Dec. 15, 1907) and Herrenschmidt (Fr. Pat. 333340, 1903) have used converters for the smelting of sulphide ores.

Methods of treating antimony ores have also been proposed by which the antimony is converted into the volatile chloride, as in Lyte's process of roasting the ore with salt. The ore may also be subjected to the action of hydrochloric acid gas in a reverberatory or muffle furnace, the volatilised chloride being condensed in a solution of hydrochloric acid (Dingl. poly. J. 250, 79–88, and 123–133).

Among processes allied to the smelting of antimony there need only be mentioned that of Herrenschmidt for the extraction of gold from antimony (Fr. Pat. 350013, 1904). This depends on the fact that when a small quantity of antimony is melted with or reduced from auriferous stibnite, all the gold present in the sulphide passes into the metal.

Many proposals have been made for the extraction of antimony by wet or electrolytic methods, but they have not been a success commercially. Reference may be made to Hering (Dingl. poly. J. 230, 253), and Borchers (Electrolytische Gewinnung des Ant. Chem. Zeit. xi. 1883, 1023).

Refining of Antimony.

Unrefined antimony contains sulphur, iron, arsenic, and sometimes copper and lead. The following analyses show the composition of typical samples, I. and II. being metal made with scrap iron, the arsenic and gold being due to admixed pyrites; III. and IV. metal from roasted ore smelted in a blast furnace:—

	I.	II.	III.	IV.
Antimony .	94·5	84·0	97·2	95·0
Iron .	3·0	10·0	2·5	4·0
Sulphur .	2·0	5·0	0·2	0·75
Arsenic .	0·25	1·0	0·1	0·25
Gold .	traces	—	—	—

All these impurities, except lead, can be removed by slagging with oxidising, sulphurising, or chlorinating agents. The usual fluxes are: Glauber salt and charcoal, which remove copper and iron as sulphides, and arsenic as sodium arsenate; and antimony glass (antimony oxysulphide) which eliminates sulphur. Chlorides, such as salt or carnallite, must be used with caution, or great loss by volatilisation may result.

Refining in crucibles finds its chief application in the English process. The 'star bowls' (*v.s.*) are cleaned from slag by chipping with sharp hammers, and the metal is then broken small and melted with 2–3 p.c. of antimony flux, prepared by melting together American potashes and powdered stibnite in varying proportions (approximately 3 parts potashes and 2 parts stibnite) until, by experiment, the correct composition is found. The refining is carried out in the pots nearest the grates, and takes 30 minutes to 1 hour, the charge for each crucible being 84 lbs. The finished product is run into 8-lb. ingots, which are carefully surrounded with slag and allowed to cool without disturbance. The coal consumption is large, but is compensated by a much smaller loss by volatilisation than occurs in other processes.

Refining in reverberatory furnaces is used at Milleschau, Bánya, Siena, and Oakland. It is imperative that the bed of the furnace should be tight and able to withstand the action of the alkali flux, and this is best attained by making it of one solid piece of soft, weathered granite. A fairly good substitute for the granite is a mixture of burnt and raw clay well rammed into an iron box. An example of such a process is that recommended by Helmhacker and used at Milleschau (Berg. u. Hütt. Zeit. 1883, 191; and Dingl. poly. J. 250, 123).

A 'glass of antimony' is prepared by fusing a mixture of the crystalline antimony oxide which collects on the hotter portions of the flues with sulphide of antimony, until it forms a glassy dark grey or brown mass; this is mixed with the carbonate for the purification of the metal, and is occasionally used alone where the metal is but slightly impure

The bed of the furnace is heated to a cherry red and 600 to 700 kilos. of crude antimony placed on it; a quantity of oxide and some arsenic escape, and in from 30 to 60 minutes the metal has run down. From 3 to 7 p.c. (according to the purity of the metal) of carbonate of soda, sometimes mixed with coal or coke, is then added. The metal is thus covered and fumes less, small jets of flame appearing occasionally on its surface; the temperature is raised, the metal remaining under the slag for from 1 to 3 hours (determined by the workman), the slag then becomes thick, and is removed by drawing it through the door with a long-handled flat transverse iron.

Three p.c. of antimony sulphide and 1½ p.c. of oxide are then thrown on the surface of the metal, and when melted 4½ p.c. carbonate of potash, or of a mixture of carbonate of potash and soda, are added. By this means the iron and last traces of sulphur are removed; in less than 15 minutes the refining is complete, and the critical operation of ladling is performed. A cast-iron hemispherical ladle, holding 15–20

kilos., is riveted to a chain hanging from the roof exactly in front of the working door, before which the cast-iron moulds for receiving the metal are arranged on a stone table. The workman dips his ladle obliquely, removing some slag with the metal; part of this is first poured into the mould to prevent the metal from actually touching the mould, and the metal is well covered with the slag and left at rest. Unless this be done the 'starring' will be imperfect, and, as this is considered a test of purity, its value will be lowered in the market. The slag may generally be used again. The oxide condensing in the flues is removed as seldom as possible, as this operation, as well as the furnace work, is very injurious to the workers.

The cost of refining 100 kilos. of regulus is from 4 to 5 shillings.

Star antimony usually contains small amounts of iron, lead, sulphur, and arsenic, but can be further purified by Liebig's method, which consists in fusing the metal successively with 12 p.c. sodium carbonate and 6 p.c. antimony sulphide, and again with sodium carbonate to which a little nitre has been added.

Unlike many other metals, antimony carries on its face its own character for purity. When 'pure,' a beautiful fern leaf or 'star' appears upon its surface, and according to the length and form of this 'star' on the ingot its quality is determined. The presence of a relatively small percentage of impurities in the metal will prevent it from 'starring.' It is this peculiar characteristic of pure antimony to crystallise on the ingot in the fern-leaf or star form when cooling, which originates the trade term of 'star antimony' for good quality of antimony.

For pharmaceutical purposes it is important to prepare antimony quite free from arsenic. This may be accomplished by Wöhler's method. A mixture of 4 parts powdered commercial antimony, 5 parts sodium nitrate, and 2 parts sodium carbonate (to prevent the formation of insoluble antimony arsenate) is thrown into a red-hot crucible. Combustion takes place quietly, the mass is pressed together and more strongly heated for half an hour, so as to become pasty without fusion, being pressed down as it rises from evolution of gas. While still hot and soft, it is removed, reduced to powder, and boiled with frequent stirring in water, the finer powder is poured off with the water, and the residue again treated, the washings being mixed with that first obtained. The water, which contains the whole of the arsenic but no antimony (Meyer), is removed from the insoluble portion by subsidence, decantation, and filtration. The residue of sodium antimonate should be white, but the presence of lead imparts a yellow colour. It is dried and fused with half its weight of cream of tartar at a moderate heat, cooled, broken into small lumps, and the potassium and sodium removed by digestion in water. The powdered metal is then fused into a button.

This method may be used quantitatively for the separation of antimony from arsenic. If the sodium nitrate be replaced by potassium nitrate, a portion of the antimony will enter into solution with the arsenic as potassium antimonate (*v.* C. Meyer, Annalen, 46, 236; Chem. Zentr. 1348, 828). Arsenic may also be completely removed by fusing the antimony in succession with 1st, potassium carbonate; 2nd, potassium nitrate; 3rd, antimonic oxide; 4th, potassium carbonate (Th. Martins, Kastn. Arch. 24, 253), or by fusing three times with fresh portions of sodium or potassium nitrate.

Duflos (Kastn. Arch. 19, 56) recommends a process in which the arsenic is driven off as fluoride by means of sulphuric acid and fluorspar. (*See* further Schw. 42, 501; also Buchner and Herberger, Repert. 38, 381, 256.)

Pure antimony may be obtained by heating tartar emetic to low redness and digesting the resultant mass in water to remove the potassium. The powder thus obtained may then be dried and fused into a button.

Tests for Impurities in Antimony.

Sulphur. The powdered metal evolves sulphuretted hydrogen gas (which blackens lead paper) on heating with strong hydrochloric acid.

Potassium or sodium. The metal is greyish and loses its lustre on exposure to air; it has an alkaline taste and reaction, and evolves hydrogen on immersion in water.

Arsenic. If deflagrated with ½ its weight of sodium nitrate, boiled with water and filtered, the arsenic enters into solution, leaving the antimony behind; the solution is saturated with sulphuretted hydrogen (if an orange precipitate, consisting of antimony sulphide, falls, this must be filtered quickly; it is due to the presence of a trace of antimony in the solution). The arsenic is deposited as the lemon-yellow sulphide on standing.

Lead and copper. The metal is powdered and treated with dilute nitric acid, evaporated nearly to dryness, taken up with water and filtered; the addition of sulphuric acid precipitates white lead sulphate, and the addition to the filtrate of potassium ferrocyanide gives a brown precipitate in presence of copper.

If sulphur as well as lead be present in the antimony, the lead is converted at once into sulphate by the action of nitric acid, the residue on evaporation is digested with yellow ammonium sulphide, which dissolves the antimonic oxide and leaves black lead sulphide.

Iron. The powdered metal is ignited with three parts nitre and washed with boiling water, the residue is boiled with hot dilute hydrochloric acid; on the addition of potassium ferrocyanide a blue precipitate is produced.

When antimony containing arsenic and iron is heated on charcoal, it gives a garlic odour and becomes coated with oxide of iron; it ceases to burn on removal of the flame, and yields a dull surface and yellow oxide (Liebig). The pure metal under such circumstances burns brilliantly and becomes coated on cooling with white crystals of the oxide.

Detection of antimony. When fused on charcoal with potassium cyanide or sodium carbonate or a mixture of the two, antimonial compounds produce a brittle white bead of metallic antimony with white fumes and a white incrustation on the charcoal; the bead leaves a white residue on treatment with nitric acid, which is soluble in cream of tartar or tartaric acid. Sulphide of antimony melts readily in the candle flame.

A delicate confirmatory test, given by Crookes, is to add to the white incrustation on

the charcoal one drop of ammonium sulphide, when the formation of the orange sulphide is conclusive evidence of the presence of antimony.

Estimation of antimony.—Fire assay. In valuing ores containing the sulphide the ore is broken into pieces about ¼ to 1 inch diameter, and from 2000 to 7000 grains of the lumps (avoiding dust), according to the probable richness of the ore, are selected. A Hessian crucible with a hole at the bottom covered with a piece of charcoal, is placed within another crucible of such size that the upper one enters about 1 inch. The ore, mixed with charcoal of about equal quantity and size, is placed in the upper crucible, covered with a layer of charcoal and luted down. Heat is then applied, the lower crucible being below the furnace bars and surrounded by ashes to keep it cool. The heat should be maintained at a cherry red, but not higher, for from 1 to 1½ hours. On cooling, the regulus is removed from the lower crucible and weighed. It should be well fused, bluish-grey, and of bright fibrous crystalline fracture, the residue in the upper crucible should be examined to see if it is free from visible sulphide. As the sulphide contains 71·8 p.c. of antimony, the percentage of available antimony in the ore may be roughly calculated.

The fire assay of an ore for metallic antimony is carried out as follows: If the ore contains sulphide, it is roasted to oxide at the lowest possible temperature in a scarifier. Oxide ores need no preliminary treatment. The charge is made up of ore, 10 grams; sodium bicarb., 25 grams; argol, 5 grams; salt to cover; and is heated carefully in a clay crucible for the shortest time and at the lowest temperature that will ensure complete reduction. The resulting metallic button is cleaned by washing, and weighed.

Wet assay.—(*a*) *Gravimetric.* The antimony is obtained in solution as antimonate or antimonite, and hydrogen sulphide is passed into the cold liquid for 20 minutes. Then, without stopping the current of gas, the solution is heated to boiling, and the gas allowed to pass for another 15 minutes. The resulting precipitate of sulphide may then be subjected to one of two methods of treatment. It may be collected on a Gooch crucible, washed with hot dilute acetic acid saturated with hydrogen sulphide and heated to constant weight at 230° in a current of carbon dioxide. Or the precipitate may be collected on a filter, washed successively with hot water, alcohol, equal parts alcohol and carbon disulphide, alcohol, and, finally, ether, and then dried. The greater part of the precipitate is transferred to a watch-glass, and that still adhering to the paper is dissolved in a little hot ammonium sulphide, and the solution allowed to run into a weighed porcelain crucible. This is then evaporated to dryness, the main portion of the precipitate added, and the whole treated with fuming nitric acid and warmed, the crucible being covered with a watch-glass. When the violent action has subsided, the contents of the crucible are evaporated to dryness, again treated with nitric acid, and finally evaporated to dryness and heated to redness till the weight is constant. The antimony is then weighed as tetroxide.

(*b*) *Volumetric.* The most important volumetric method is that of Möhr, in which antimony trioxide or any antimonious compound is dissolved in a solution of tartaric acid, neutralised with sodium carbonate, treated with a cold saturated solution of sodium bicarbonate in the proportion of 10 c.c. to each 0·1 gram Sb_2O_3, and quickly titrated with $N/10$-iodine solution, using starch as indicator.

(*c*) *Electrolytic.* Classen and others have shown that if antimony sulphide (*v.s.*) is dissolved in the minimum amount of concentrated solution of sodium sulphide, and treated with excess of sodium sulphite, or, better, potassium cyanide solution (to destroy polysulphides), the liquid can be successfully electrolysed in the cold with a current of 0·25–0·5 amp., using a platinum dish as cathode. The process takes about 12 hours, and gives a good coherent deposit of metal which can be washed with water, alcohol, and ether, and finally dried and weighed.

Properties of Antimony.

Antimony is a lustrous, bluish-white metal, which has a coarsely laminated or granular structure, according as it has been slowly or quickly cooled. By partial solidification it can be obtained in obtuse rhombohedra, approximating to cubes.

The sp.gr. of the metal is 6·72–6·86. It melts at 630·5°C. (Heycock and Neville, Chem. Soc. Trans. 1895, 186), and boils at about 1350° in a current of hydrogen. Antimony has a hardness of 3–3·5, and is so brittle that it can readily be powdered. It is a bad conductor of heat and electricity.

The most important physical property of antimony is that of expanding on solidification, a property possessed also by its alloys. At the ordinary temperature it is not acted on by the air, but oxidises quickly on melting, and burns at a red heat, producing white fumes of the trioxide. It is oxidised by nitric acid of various strengths, dilute acid producing principally the trioxide, and the concentrated acid producing the pentoxide (H. Rose, Analyt. Chem. 1, 258). Dilute sulphuric and hydrochloric acids are without action on it, but the strong acids produce the sulphate and chloride respectively. When fused with borax or other vitrifying material, it imparts to them a yellow colour.

Antimony combines directly with the halogens with evolution of light and heat, and also, at a higher temperature, with the elements of the sulphur group, and with phosphorus and arsenic. The element occurs in three modifications: (1) the crystalline or ordinary form described above; (2) an amorphous yellow modification, soluble in carbon disulphide, which is produced by the action of oxygen on liquid stibine at −90°; and (3) the amorphous explosive antimony, which is best prepared by the action of a weak constant electric current on a concentrated acid solution of antimony trichloride, the strength of current bearing a constant relation to the surface of deposition, not less than ½ grain being deposited per sq. inch per hour. Thus produced, it is bright and steel-like in appearance, with an amorphous fracture, and sp.gr. 5·78. When heated to 200°, or struck or scratched, it rapidly changes into the crystalline form, increasing in density, with

the production of great heat. Antimony trichloride is always contained in the metal to the extent of 4·8–7·9 p.c., and is given off when the form changes. It is probable that this substance is a solid solution of an antimony halogen compound in an allotropic form of antimony, and that the explosion consists in the rapid transformation of the latter into the stable form. The change is accompanied by an evolution of heat amounting to 20 cals. per gram. Cohen and others (Zeit. physikal. Chem. 1904, 47, 1; 1905, 50, 291; 52, 129) have shown that this change goes on slowly when explosive antimony is preserved.

Antimony is precipitated as a fine powder by the action of zinc on an acid solution of an antimony salt. In this form it is sold as 'iron black' for producing an appearance of polished steel on papier maché, plaster of Paris, and zinc ornaments.

Brass can be covered with a fine lustrous coating of antimony by dipping in a hot mixture of 1 part tartar emetic, 1 part tartaric acid, 3 or 4 parts powdered antimony, 3 or 4 parts hydrochloric acid, and 3 parts water.

It may be deposited electrolytically on brass or copper by using a bath of the double chloride of antimony and ammonia acidulated with hydrochloric acid.

Alloys of Antimony.

Antimony alloys with most of the heavy metals and with the alkaline metals. It generally increases the fusibility, brittleness, and hardness of the metals with which it is combined, and imparts the valuable property of expanding on solidification, thus producing very fine impressions. The alloys of silver, gold, and lead with antimony have a greater density than the mean of the constituents, while those of iron, tin, and zinc are of less density. The sharpest impressions are produced when any of these alloys are cast at a low temperature (J. Soc. Chem. Ind. 1, 982). The castings are usually made in brass moulds coated with lampblack and turpentine.

With *lead*, antimony mixes readily in all proportions. By the addition of antimony to red-hot lead, alloys which crystallise in rhombohedra have been obtained by F. de Jussieu (Compt. rend. 38, 1321–1322). An alloy of equal parts of lead and antimony is very brittle, and rings when struck. Nasmyth has recommended the addition of 5 p.c. antimony to lead for use instead of bronze in taking casts of works of art (Athenæum, No. 1176, 511).

Type metal is essentially an alloy of lead and antimony, frequently with addition of tin and containing less frequently bismuth or copper. A few examples of common type-metals are:

	Lead	Antimony	Tin	Copper	Bismuth
Type metal .	55	30	15	—	—
„ .	70	18	10	2	—
„ .	50	28	—	—	22
Stereotype plate	85·7	14·3	—	—	—
„ „ .	70	15	—	—	15
Linotype metal	84·5	13·5	2	—	—

Wetterstedt's patent ship sheathing consists of 100 lead to about 3 antimony, but does not appear to have been used to any extent. The alloy, containing varying proportions of antimony, is also used, under the name of hard lead, in lead pipes, for making pumps and taps for raising acid in alkali works, in the manufacture of cannon-balls and shot, and for the emery wheels and tools of the lapidary.

Tin forms numerous useful alloys with antimony, especially with the addition of other metals. *Common Britannia metal* consists of tin 140, copper 3, antimony 9. Britannia metal for castings: tin 210, copper 4, antimony 12; ditto for lamps: tin 300, copper 4, antimony 15. The best Britannia metal contains tin 90, antimony 10, lead and bismuth being carefully excluded. Copper also is never added except for the production of colour. The exact proportion of antimony used depends on the quality of the tin, and is always ascertained experimentally. Increasing the proportion of antimony raises the m.p., increases the hardness, and decreases the malleability of the alloy. Good alloys take a brilliant polish, and show a fine-grained, jagged fracture. The presence of arsenic in the antimony diminishes the ductility of the product (*v.* BRITANNIA METAL). Superior pewter is made by fusing together tin 12, copper 1, antimony 1.

Metal argentum contains tin 85·5, antimony 14·5.

Ashbury metal: tin 77·3, zinc 2·8, antimony 19·4. Ships' nails, tin 3, lead 2, antimony 1.

Minofer is tin 68·5, antimony 18·2, copper 3·3, and zinc 10.

Bearing or *anti-friction metal* usually contains antimony, tin, and copper, but the composition is very variable, and some cheap varieties consist chiefly of iron or zinc. Occasionally lead and tin or lead and zinc are alloyed with antimony to form bearing metals. As the name indicates, it is used for machinery bearings, being especially suitable for light loads at high speeds. As examples of these alloys the following may be given:—

	Antimony	Tin	Copper	
Babbit's metal .	8·3	83·3	8·3	—
Very hard bearings .	—	5	2·5	Iron 70
Cheap bearings .	—	1·7	7	Zinc 90
U.S. Rly. Babbit metal	7·4	88·9	3·7	—
German Rly. Babbit metal . .	11·1	88·3	5·6	—

Copper. The presence of 0·15 p.c. of antimony renders copper both cold and hot short. With varying proportions of the two metals, shades from pure copper-red to rose-red, crimson, and violet may be obtained, the last when equality is reached. Two definite compounds of copper and antimony appear to exist, viz. $SbCu_2$, a violet alloy known as 'Regulus of Venus,' and $SbCu_4$ (Kamensky, Phil. Mag. [5] 17, 270; *v.* also Ball, Chem. Soc. Trans. 1888, 167).

Antimony is frequently added to brass to heighten its colour. These alloys are harder and finer in texture than copper or brass, and take a better polish. Antimony is sometimes added for this reason to the material for concave mirrors. It is also added occasionally to bell metal, as it is believed to add to the intensity and clearness of the sound. Many celebrated old bells contain antimony, *e.g.* 'Old Tom' of Lincoln, which contains about 0·03 p.c.

Zinc. Antimony forms definite crystalline compounds with zinc, which, however, differ widely in composition while retaining the same

form. They decompose water rapidly at the boiling temperature, and this action is promoted by the presence of traces of platinic chloride. Cooke has suggested the suitability of this reaction for the preparation of pure hydrogen.

Iron containing less than ¼ p.c. of antimony is both hot and cold short. A mixture of 7 parts antimony and 3 parts iron heated to whiteness with charcoal forms a hard white alloy which strikes sparks with steel.

Alloys of *antimony* and *aluminium* have been described by Pécheux (Compt. rend. 138, 1606), which vary in composition from $SbAl_{30}$ to $SbAl_{40}$, having a density of 2·73–2·60, and m.p. 760°–730°. These alloys expand on solidifying, and are hard, but fairly malleable. They are unaltered by air or water at ordinary temperatures, and this property, combined with their lightness and malleability, should render them useful in the building of light structures such as aeroplanes.

Melted gold absorbs the vapour of antimony, but gives it up almost entirely on further heating. Gold loses its malleability when $\frac{1}{2000}$ of antimony is present. An alloy of 9 gold and 1 antimony is white and very brittle, with an amorphous porcelain-like fracture. Silver antimonide occurs as the mineral *discrasite*.

Compounds of Antimony.

The principal compounds of antimony are formed by combination with oxygen, sulphur, and chlorine; some compounds contain two of these negative elements, of which the oxychloride or *powder of Algaroth*, and the oxysulphide or *glass of antimony* are examples.

The most important of these are the trichloride, trisulphide, and trioxide.

Antimony trisulphide Sb_2S_3.

Crude antimony, antimony ore, sesquisulphide of antimony; Schwefelspiessglanz; Grau-Spiessglanzerz; Stibium sulphuratum nigrum; lupus metallorum.

This substance, as it occurs naturally, or after liquation, is usually too impure to be employed for other purposes than the preparation of the metal.

The ordinary sulphide may be prepared by the following methods:—

(1) Thirteen parts pure antimony are mixed with 5 parts flowers of sulphur, and projected in portions into a red-hot crucible; when completely fused, it is poured out and any free metal detached.

(2) Sulphuretted hydrogen precipitates it as an orange precipitate from a solution of an antimony salt.

(3) Digest for two hours in a closed vessel 1 part crude antimony sulphide, 1 part pearl ash, 1½ parts lime, and 15 parts water, and add sulphuric acid; the alkaline sulpho- salt first formed is decomposed by the acid with the precipitation of the pure sulphide. Antimony sulphide is soluble in alkaline sulphides and in acid potassium sulphate. When finely powdered and rubbed to a paste at 20° or 30° with strong sodium sulphide solution, a coppery metallic mass is produced, and the liquor, on addition of more sodium sulphide, yields Schlippe's salt.

The sulphide is used to some extent in refining gold from silver and copper, and in the preparation of safety matches and percussion pellets for cartridges, in pyrotechny and in veterinary surgery.

Kermes mineral. *Brown-red antimony sulphide. Pulvis Carthusianorum. Sulph. stibiatum rubrum.*

Kermes mineral usually consists of a mixture of the trisulphide and trioxide containing alkali. Berzelius and Rose state that some samples examined by them consisted of a true double sulphide of potash and antimony.

Preparation.—Fuchs asserts that if antimony sulphide is heated and *suddenly* cooled in water it yields an orange-red, less dense powder of kermes. A. Ditte (Compt. rend. 102, 212) does not confirm this statement.

(1) Four parts pure potassium carbonate and 11 parts pure antimony sulphide are heated to fusion in a covered crucible, cooled, boiled with water, and filtered. The solution on exposure to the air deposits kermes, the residue from the first boiling is heated with the mother liquor from some previously deposited kermes, and yields a further quantity; this operation is repeated until an insoluble residue of trisulphide and trioxide is left. Each successive deposit of the kermes contains a larger amount of the oxide.

(2) Fuse together 2 parts antimony, 1 sulphur, and 3 sodium carbonate; or, 1 antimony sulphide and 3 or 4 tartaric acid, until fumes cease to be evolved; and treat the product as in (1).

(3) The slags from the reduction of antimony ore with cream of tartar slowly precipitate kermes when treated with water; this is sold to veterinary surgeons as 'kermes by the dry way.' When antimony sulphide is boiled with potash and precipitated with an acid, the kermes produced contains no oxide (Liebig). The kermes produced by the action of *dilute* alkaline carbonate on antimony sulphide also contains no oxide (Rose). The oxide may be removed from ordinary kermes by digestion with tartaric acid. A solution containing so much alkali as to give no precipitate on cooling gives, when treated with carbonic acid gas, a highly sulphurated kermes containing antimony pentasulphide.

Kermes is a brown-red, loosely coherent powder, with a brown streak, containing water, which is given off below 100°. It is lighter than the ordinary sulphide. The kermes containing antimony oxide, when fused and solidified, is destitute of crystalline structure, while that free from oxide produces a highly crystalline solid.

Antimony pentasulphide Sb_2S_5. *Golden sulphide of antimony; sulphur antimonii auratum.*

Prepared by boiling the trisulphide with potash and ground sulphur, filtering and precipitating with acid. Redwood recommends 4 parts black antimony sulphide, 8 lime, and 80 water, digested, filtered, and precipitated with hydrochloric acid; or, 2 sulphide, 4 potassium carbonate, and 1 sulphur, to be fused, treated with 20 parts water, filtered, and the solution precipitated with a large excess of sulphuric acid.

On treating the mother liquor from kermes mineral with an acid, the pentasulphide is precipitated with evolution of sulphuretted hydrogen. The mother liquor from Schlippe's salt also yields this substance on the addition of an acid (R. Bartley, Chem. Soc. Trans. 1876, 1, 748). It generally contains free sulphur.

Antimony pentasulphide is of some importance commercially, as it is used in the process of vulcanising rubber.

Antimony pentasulphide combines with alkaline sulphides, forming sulphantimonates, which as well as the sulphantimonites (which contain less sulphur) are known as 'livers of antimony.' Of these the sodium sulphantimonate, or *Schlippe's salt*, is the most important.

A mixture of 11 parts finely powdered antimony trisulphide, 13 crystallised sodium carbonate, 1 flowers of sulphur, 5 recently slaked lime, and 20 water, is digested at the ordinary temperature for 24 hours with frequent stirring, in a vessel which can be closed. It is then strained and washed several times with water, the solution and washings are evaporated in a porcelain or clean iron dish until a sample yields crystals on cooling; the solution is then cooled, and the resultant crystals washed with cold water and dried in the open air or in a desiccator at the ordinary temperature. The salt is more rapidly formed when the mixture is heated (Liebig, Handwörter. d. Chem. 2te Aufl. 2, 139; also Gm. 4, 384).

Oxysulphides of antimony are formed by the combination of the sulphides and oxides or by the partial oxidation of the sulphides.

Antimony crocus or saffron. Fuse together 3 parts of antimony trioxide and 1 part trisulphide, or fuse the oxide with the calculated quantity of sulphur.

The scoria from the fusion of the sulphide with carbon and alkaline carbonate in the preparation of the metal is known as crocus of antimony.

Crocus of antimony is a brownish-yellow body.

Glass of antimony. Vitrum antimonii. When antimony sulphide is fused until the necessary amount of sulphide has been converted into oxide, the whole forms a glassy mass of this compound. The best method of preparation is to roast the sulphide completely into oxide and fuse the product with $\frac{1}{20}$ part of sulphur. Its colour varies with the proportion of sulphur present from yellowish-red to hyacinth red. The best quality is of a fine red colour, and contains 8 antimonious oxide and 1 antimonious sulphide.

Antimony cinnabar is an oxysulphide of a fine vermilion colour, soft and velvety, and unaltered by air or light; it is used in the preparation of oil and water colours, and in calico-printing. It is prepared by dissolving antimony oxide in hydrochloric acid, and placing the solution in a large wooden tub which is $\frac{2}{3}$ filled with calcium hyposulphite. The mixture is stirred and heated with steam to 70°, the precipitate soon subsides as a yellowish sediment which changes to a bright orange-red, and is thoroughly washed, and dried below 50°. N. Teck (Chem. Zentr. 26, 1880) prepared it from 4 parts tartar emetic, 3 tartaric acid, 18 water mixed at 60° with hyposulphite of soda and heated to 90° (Wagner), or 4 volumes antimonious chloride of sp.gr. 1·19 mixed with 10 vols. water and 10 vols. hyposulphite of 1·19 sp.gr., and heated gradually to 55° (Mattieu Blessy).

Antimony yellow (Mérimée's yellow). According to the method of Mérimée, a mixture of 3 parts bismuth, 24 parts antimony sulphide, and 64 parts nitre, is thrown little by little into a heated crucible, fused, powdered, washed, and dried. In this way bismuth antimonate is produced. Of this 1 part is mixed with 8 parts ammonium chloride and 128 parts litharge, and fused as before. The time occupied and the temperature used cause considerable variations in the colour. Mérimée's yellow is a fine permanent colour of good body. It is only used for the finest painting.

Naples yellow is essentially an antimonate of lead containing excess of lead oxide, but mixtures of carbonate and chromate of lead are also sold under the name. Many processes may be used for its preparation. According to Brunner, a mixture of 1 part tartar emetic, 2 parts lead nitrate, and 4 parts sodium chloride is heated, just to fusion, for 2 hours. The cooled mass is placed in water and soon falls to pieces. According to Guimet, it may be produced by heating a mixture of 1 part potassium antimonate and 2 parts red lead. It is a fine very permanent orange or yellow pigment, used in oil-painting, and, mixed usually with a lead glass, for glass and porcelain staining.

Antimony trichloride (*Butter of antimony*).

Prepared by dissolving the sulphide in strong hydrochloric acid with a small quantity of nitric acid and evaporating to dryness.

To prepare the pure chloride, the acid solution is evaporated until it just crystallises on standing in a cool place; it is then transferred to a retort and distilled until a drop of the distillate solidifies on a cold surface; the receiver is then changed, and the further distillate is pure.

It is a white, buttery, semivitreous, deliquescent solid. When pure, it is crystalline, and melts sharply at 73·2°, and boils at 223·5° (Beckmann, Zeitsch. anorg. Chem. 1906, 51, 96). It is used as a caustic in medicine, for the preparation of tartar emetic, and as a 'bronzing solution' for gun-barrels, &c. For this purpose a saturated solution is mixed with olive oil, rubbed over the warmed metal and exposed to the air until the proper colour is produced. When bronzed, the metal is polished with a burnisher or with wax, or coated with a varnish of 2 oz. shellac, 3 drachms dragon's blood, dissolved in 2 quarts of methylated spirit.

Antimony oxychloride. *Basic chloride, powder of Algaroth; pulvis Algarothi; S. Argelicus; mercurius vitæ, &c.*

Water is added to a solution of the trichloride until it is distinctly turbid, when it is filtered (the precipitate carries down any traces of sulphuretted hydrogen which may be present, and which if left would soon turn the substance yellow). Five to ten volumes of water are added, and the precipitate is washed with cold water and filtered. Its composition varies with the temperature at which it is produced and the amount of water used, varying between SbOCl and, where a very large amount of water has been used, Sb_2O_3. It is a white powder, and is principally used for the preparation of pure antimonious oxide and tartar emetic.

Antimonious oxide Sb_4O_5. *Trioxide of antimony.* If antimony is powdered and heated in a shallow dish, it eventually forms antimony tetroxide Sb_2O_4; this, together with the unchanged metal, is fused in a crucible, when

the tetroxide and antimony react, forming antimonious oxide, the excess of antimony sinking to the bottom of the crucible.

For pharmaceutical purposes 20 parts of finely powdered antimony sulphide are gradually added to 100 parts hydrochloric acid containing 1 part nitric acid, and heated, gently at first, and then more strongly, until sulphuretted hydrogen ceases to be evolved. It is then boiled for an hour, enough water is added to produce a slight precipitate, which removes the last traces of sulphuretted hydrogen, and filtered into a vessel containing 1 gallon of water, precipitating the oxychloride, which is filtered and washed until it ceases to have an acid reaction; it has then become converted into the trioxide.

It is a white fusible solid, slightly soluble in water, volatile at a red heat. It becomes further oxidised to the tetroxide Sb_2O_4 on heating in air, and is then non-volatile.

In presence of alkalis it absorbs oxygen; for this reason it has been proposed to use it for reducing nitrobenzene to aniline, and in the preparation of aniline red.

It is used for the preparation of tartar emetic. When ground with linseed oil it is sometimes used as a substitute for white lead, being less injurious to the workmen and less acted upon by sulphur gases; it has, however, less 'body' and is more expensive.

Tartar emetic. *Potassium antimony tartrate. Tartarus stibiatus. Brechweinstein; spiessglanzweinstein.* $2C_4H_4K(SbO)O_6,H_2O$. Three parts antimonious oxide and 4 cream of tartar are made into a thin paste with water and digested for about half an hour, keeping the water at constant volume; 8 parts of water are then added, boiled, and filtered whilst hot. The oxychloride or oxysulphide may be substituted for the oxide, but not so satisfactorily.

Tartar emetic forms octahedral crystals, which give off a part of their water on exposure to the air. They dissolve in 14·5 parts cold and in 1·9 parts boiling water. They show an acid reaction with litmus, and have a nauseous metallic taste, 5–10 centigrams causing vomiting, and larger quantities being very poisonous.

It is used in medicine and in the preparation of pomades, &c., and also largely as a mordant in dyeing and calico-printing. Mixtures of tartar emetic for mordanting are sold containing as much as 33–59 p.c. zinc sulphate at a lower price, under the names *tartar emetic powder, tartar emetic substitute, antimony mordant*, &c. It is known that zinc acetate may partly replace the tartar emetic with advantage, but the sulphate appears to be a simple adulterant (H. Smid, Chem. Zeit. 1882, 949).

Several other compounds of antimony have been proposed for mordants instead of tartar emetic. E. Jacquet (Dingl. poly. J. 257, 168) advised the use of a mixture of basic antimony oxalate with twice its weight of ammonium oxalate. Nölting recommended the double oxalate of potash or of ammonia and antimony (Dingl. poly. J. [3] 255, 122). It is stated that the latter compounds have long been used under other names.

The use of the fluoride (which is not precipitated with excess of water) and the double fluorides of antimony and the alkalis has been patented by S. M'Lean. Watson, jun., patented a process for using trichloride with sufficient common salt to prevent the precipitation of the oxychloride (G. Watson, J. Soc. Chem. Ind. 1886, 5, 591; B. W. Gerland, J. Soc. Chem. Ind. 1884, 4, 643; and Kopp and Bruère, J. Soc. Chem. Ind. 1888, 566). A double salt of antimony fluoride and ammonium sulphate $SbF_3.(NH_4)_2SO_4$, known as 'antimony salts,' is also used in dyeing, but as it attacks glass as well as metal, it should be stored and worked in wooden vessels. A good bath is 100 litres water, 400 grams antimony salts, 200 grams soda crystals, at a temperature of 50° (Frey, Bull. Soc. Md. Mulhouse, 1888, 301).

Tartar emetic as a mordant has, at the present time, been largely superseded by the double oxalate of potassium and antimony, as it is cheaper than the tartrate, and equally efficient, although it contains less antimony.

Recently F. Düring has recommended the use of the double lactate of antimony and calcium, which can readily be obtained by mixing, in the dry state or in solution, alkali lactates with 'antimony salts,' or other antimonious compounds (Färber, Zeit. [20] 319). He states that at least 80 p.c. of the antimony in the solution will actually go into the cloth as mordant.

ANTIMONY SALTS. A compound of antimony fluoride with ammonium sulphate used as a mordant (*v.* ANTIMONY).

ANTINONIN. Trade name for a solution of potassium *o*-dinitrocresol used as a fungicide.

ANTIPYRINE. *Phenyldimethylpyrazolone* (*v.* PYRAZOLE).

ANTIRRHINIC ACID *v.* DIGITALIS.

ANTISEPTICS *v.* DISINFECTANTS.

ANTISEPTINE. Said to be a mixture of zinc iodide, zinc sulphate, boric acid, and thymol.

ANTISEPTOL. *Cinchonidine iodosulphate*, used as a substitute for iodoform.

ANTITHERMIN. *Phenylhydrazone* of *lævulic acid* $CH_3{\cdot}C(N_2H{\cdot}C_6H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ is obtained by dissolving phenylhydrazine in dilute acetic acid, adding an aqueous solution of the equivalent quantity of lævulic (acetopropionic) acid, and crystallising the resulting yellow precipitate from alcohol (Farbw. vorm. Meister, Lucius & Brüning in Höchst a. M., Ger. Pat. 37727).

It forms colourless, inodorous, and tasteless scales, melts at 98°–99°, is sparingly soluble in cold water, soluble in alcohol, ether, or dilute acids. It has been employed as an antipyretic (Nicot, Chem. Zentr. 1887, 415); but, according to Stark (Chem. and Drug, 32, 651), its use in medicine is now almost abandoned. Inasmuch as it is decomposed by alkalis, its physiological activity is probably due to phenylhydrazine (Gehe & Co., Chem. Zentr. 1888, 49).

ANTWERP BROWN *v.* PIGMENTS.

ANVULA *v.* AMLAKI.

AOOD-I-BALSAM. *Balsaam of Mecca* (*v.* OLEORESINS).

APATITE. A crystallised mineral, consisting of calcium phosphate in combination with fluorine, chlorine, hydroxyl, or carbonic acid, the formula being $(CaF)Ca_4(PO_4)_3$ or $3Ca_3(PO_4)_3 + CaF_2$, where F may be replaced by Cl, OH, or CO_3. There are thus several chemical varieties, namely, fluor-apatite, chlor-apatite, hydroapatite, and carb-apatite; the last being also

called podolite (W. Tschirwinsky, 1907). Similarily, by partial replacement of the calcium, there are the chemical varieties mangan-apatite, cupro-apatite, and talc-apatite. In addition to these, some other trivial names are applied to varieties of crystallised apatite; for example, asparagus-stone, from Murica in Spain; moroxite, from Arendal in Norway; and francolite, from Wheal Franco, near Tavistock in Devonshire. The distinction between fluor-apatite and chlor-apatite is, however, the only one of any importance. (For the varieties of massive apatite, *v.* PHOSPHORITE.)

Apatite is often found as well-developed crystals. These belong to the hexagonal system, and are usually bounded by a six-sided prism and pyramid with the basal plane, though sometimes numerous other brilliant facets are present. The colour is commonly greenish or brownish, but sometimes sky-blue, violet, or colourless. The crystals may be transparent or opaque, and they have a vitreous to sub-resinous lustre. Sp.gr. 3·2; hardness 5 (the mineral can be scratched with a knife). Owing to its variable appearance, apatite is frequently mistaken for other minerals, and it well deserves its name, from *ἀπατᾶν*, 'to deceive.' In determining the mineral, it is always well to test for phosphoric acid.

As microscopic crystals, apatite is present as an accessory constituent of igneous rocks of all kinds. It also occurs in metamorphic rocks and in metalliferous veins. Fine specimens are found at many localities, but only in two regions—in Norway and Canada—is crystallised apatite mined for commercial purposes. In southern Norway, in the neighbourhood of Kragerö and Bamle, extensive deposits of chlor-apatite occur in connection with gabbro (a pyroxene-felspar rock of igneous origin). Large deposits of fluor-apatite are mined in Ottawa Co., Quebec, and in Renfrew Co., Ontario; here the mineral forms beds in Laurentian gneiss, usually in association with crystalline limestone.

L. J. S.

APERITOL. A mixture of equal parts of valerianyl and acetylphenolphthaleïn, used as a laxative.

APHTHITE. An alloy containing 800 parts of copper, 25 of platinum, 10 of tungsten, and 170 of gold (Zeits. f. d. C. Grossgew. 4, 313).

APIGENIN *v.* FLAVONE.

APIIN. A glucoside contained in parsley and celery, forming on hydrolysis *apigenin* and a disaccharide, made up of α-glucose and a pentose, *apiose* (Vongerichten, Annalen, 1901, 121), (*v.* FLAVONE and GLUCOSIDES).

APIOL *v.* OILS, ESSENTIAL.

APIOSE *v.* CARBOHYDRATES.

APIOS TUBEROSA (Moench.), *Glycine apios* (Linn.). A leguminous plant from North America, the roots of which have been proposed as a substitute for the potato, and the young seeds for peas. Payen (Compt. rend. 28, 189) gives the following analysis of the root: Nitrogenous matters, 4·5; fatty matters, 0·8; starch, sugar, &c., 33·55; cellulose, &c., 1·3; inorganic, 2·25; water, 57·8 (*cf.* Brighetti, Chem. Zentr. 1900, i. 914).

APIUM *v.* OILS, ESSENTIAL.

APIUM PETROSELINUM (*Carum petroselinum*) *v.* FLAVONE.

APOLLO RED *v.* AZO- COLOURING MATTERS.

APOMORPHINE *v.* VEGETO-ALKALOIDS.

APOPHYLLITE *v.* CALCIUM.

APOREINE. A poisonous alkaloid found in the juice of *Papaver dubium*. Gives crystalline salts. The hydrochloride $C_{18}H_{16}NO_2$,HCl, forms silvery nacreous scales, subliming without decomposition in dry carbon dioxide between 220° and 240°.

APORETIN *v.* RHUBARB.

APOTURMERIC ACID *v.* TURMERIC.

APPLE. The fruit of *Pyrus malus*. Many varieties are known, differing greatly in size, shape, colour, and flavour.

The solid matter of apples consists largely of sugars—glucose and sucrose; their acidity is due to malic acid $C_2H_4O(COOH)_2$. In unripe apples starch is present—sometimes to the extent of 4 or 5 p.c., but the fully ripened fruit is devoid of starch. Cellulose forms about 1 p.c. of the weight of the ripe fruit, pentosans about 0·5 p.c., and pectose matters also about 0·5 p.c. Mineral matter is usually between 0·2 and 0·3 p.c., and about half of this is potash.

The following analyses of American Baldwin apples show the changes which occur during ripening:—

	Very green	Green	Ripe	Over-ripe
Water	81·33	79·81	80·36	80·30
Solids	18·67	20·19	19·64	19·70
Reducing sugars	6·40	6·46	7·70	8·81
Cane sugar	1·63	4·05	6·81	5·26
Starch	4·14	3·67	0·17	none
Free malic acid	1·14	—	0·65	0·48
Ash	0·27	—	0·27	0·28

The following figures relate to South-African apples (Ingle). The flesh and rind of the ripe fruit, the core and pips being rejected, contained:—

Variety	Koo	Reinette de Canada	Northern spy	Versfeld	Lord Wolseley
Water	85·08	—	82·64	87·65	84·41
Dry matter	14·92	—	17·36	12·35	15·59
Ash	0·313	—	0·262	0·270	0·268
Acidity (as malic acid)	0·47	0·65	0·48	0·71	0·47
Reducing sugars	7·44	6·87	10·26	9·43	10·85
Cane sugar	4·63	3·68	4·77	1·36	1·58
Nitrogen	0·046	0·094	0·058	0·057	0·043
Crude fibre	1·33	1·24	1·26	—	0·88
Per cent. in ash:					
Potash	54·48	—	48·52	53·30	51·58
Lime	2·63	—	1·95	1·82	2·70
Silica	1·51	—	1·58	1·25	0·90
Phosphorus pentoxide	11·15	—	12·10	8·09	12·16
Sulphur trioxide	2·46	—	2·67	3·13	3·10
Chlorine	0·50	—	0·89	1·02	1·00

The proportions of lime found in these apples are apparently lower than those usually found

in American apples, while the figures for phosphorus pentoxide and chlorine are higher.

Hotter (Chem. Zentr. 1900, ii. 484) gives the following analysis of apple ash :—

K_2O	CaO	MgO	Fe_2O_3	SiO_2	SO_3	P_2O_5
51·58	4·22	3·71	1·18	1·08	2·49	10·42

Certain varieties of apples—particularly those used for cider-making—are rich in tannin, and, when the cells are broken, *e.g.* by cutting the apple or by a bruise, so as to admit air, a browning takes place—probably by the action of an oxydase upon the tannin.

Otto (Bied. Zentr. 1901, ii. 553 ; and 1902, 31, 107) found that the percentage of water increases during ripening on the tree, but diminishes on storing, that the starch diminishes and finally disappears, while the cellulose remains constant. The nitrogen increases during ripening on the tree, but afterwards diminishes. The acidity diminishes during ripening, both before and after gathering.

Under normal conditions, the starch present in unripe apples is converted, during ripening, into sugar by the diastase present, but if the unripe apples be bruised, this change is incomplete in the bruised portion, and starch may be found in the browned tissues. According to Warcollier (Compt. rend. 1905, 141, 405), this is due to the paralysing effect upon the diastase of the tannin which escapes from the bruised cells (and which, by the action of an oxydase, gives rise to the browning), thus preventing the saccharification of the starch, upon which normal ripening depends.

Apples are now dried by artificial heat (with or without the use of sulphur dioxide, which improves the colour), and sold, either as whole fruit or as 'apple rings.' Fresh apples yield about one-seventh of their weight of the dried product. Zinc is frequently found in dried apples, probably from contact with zinc trays during the drying process. As much as 0·58 gram Zn per kilogram has been found in American dried apples. American analyses give as the average components of dried apples : 36 p.c. water, 1·4 p.c. protein, 3·0 p.c. ether extract, 57·6 p.c. carbohydrates, and 1·8 p.c. ash. The flavour, and particularly the odour, of apples can be imitated by *iso*-amyl-*iso*-valerate dissolved in spirits of wine. This constitutes the 'essence of apples' used in confectionery and perfumery.

H. I.

APPLES, ESSENCE OF, *v.* APPLES.

APPLE TREE. (*Pyrus malus*, L. ; *Pomme*, Fr. ; *Apfel*, Ger.) The wood is much used in turnery, and that of the crab tree is used by millwrights for the teeth of mortice wheels. The bark contains a tannin identical with that contained in horse-chestnut bark.

APRICOT. The fruit of *Prunus armeniaca* (Linn.).

The following analyses were made by Fresenius :—

		I. Medium size	II. Large wt. 60 grams.
	Sugars	1·14	1·53
Soluble	Free acid	0·90	0·77
	Nitrogenous matter	0·83	0·39
	Pectins, gum, &c.	5·93	9·28
	Ash	0·82	0·75
Total soluble matter		9·62	12·72
Insoluble	Seeds (stone)	4·30	3·22
	Skin and cellulose	0·97	0·94
	Pectose	0·15	1·00
	Ash	(0·07)	(0·10)
Total insoluble matter, excluding ash		5·42	5·16
Water		84·96	82·12
		100·00	100·00

In Californian-grown apricots, Colby (Exp. Stat. Record, 1893, 4, 918) found, in the whole, fresh fruit, water, 85·16 ; dry matter, 14·84 ; containing nitrogen, 0·194 ; sugar, 11·10 ; ash, 0·49.

The ash was found to contain :

K_2O	Na_2O	CaO	MgO	MnO_2	P_2O_5	SO_3	SiO_2
59·36	10·26	3·17	3·68	0·37	13·09	3·63	5·23

Cl	Fe_2O_3
0·45	1·68

Californian apricots appear to contain more nitrogen than the European fruit. As many other analyses agree in giving about 11 p.c. of sugar, it is probable that some error has been made in Fresenius' figures, though they have been widely quoted.

The sugar is chiefly sucrose, with a little dextrose, and invert sugar, which becomes less when the fruit ripens (Desmoulière Ann. Chim. anal. 1902, 7, 323). The colouring matter is probably related to carrotene.

The acidity of apricots is chiefly due to malic and citric acids.

The kernels of apricot 'pits,' or stones, like those of the other members of the *Prunus* family, contain amygdalin and about 40 p.c. of a fatty oil resembling almond oil. This oil has a sp.gr. of 0·9204 at 15·5°, a pale-yellow colour, and a slight odour of almonds (Maben, Pharm. J. Trans. [3] 16, 797). More recent determinations give the following (Dieterich, Chem. Zentr. 1902, 2 [15], 943) : sp.gr. at 15°C. 0·915–0·921, at 90°, 0·9010–0·9015 ; solidifying point, −14° to −20° ; saponification value, 193·1–215·1 ; iodine value (Hübl), 100–108·7 ; refractometer value at 25°, 65·6–67·0 ; at 40°, 58·0 ; at 50°, 52·25. It can be distinguished from almond oil by Biber's reagent (fuming nitric acid, sulphuric acid and water), with which it gives a red colour, while almond oil only yields a faint yellow.

The flavour of apricots can be imitated by a mixture of *iso*amyl butyrate and *iso*amyl alcohol.

Dried apricots are prepared either by sun-drying or by artificial heat, sulphur dioxide being often employed in the latter case, in order to prevent darkening in colour. They are largely used in America and in some of the colonies. American analyses show them to contain about 32 p.c. of water, 63 p.c. of carbohydrates, 2·9 p.c. of nitrogenous matter, and 1·4 p.c. of ash.

H. I.

APRICOT, ESSENCE OF. A mixture of *iso*amyl butyrate and *iso*amyl alcohol.

APRICOT KERNEL OIL *v.* ALMOND OIL.

AQUA FORTIS *v.* NITRIC ACID.

AQUA REGIA. *Nitromuriatic acid ; Königswasser.* A name given by the alchemists to a mixture of nitric and hydrochloric acids, originally prepared by dissolving sal ammoniac in strong nitric acid, and used by them as a solvent for gold, sulphur, &c. Usually made

by mixing 1 vol. of nitric acid with 4 vols. of hydrochloric acid. The mixture is at first colourless, but gradually—especially on heating—acquires a deep orange-yellow colour, due to the formation of nitrosyl chloride and free chlorine: $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$. The solvent action of aqua regia appears to be mainly due to the free chlorine.

AQUA VITÆ. An alchemistic name used to denote common alcohol as obtained by distilling a liquid which has undergone vinous fermentation.

ARABIC GUM *v.* GUMS.

ARABINOSE *v.* CARBOHYDRATES.

ARACHIDIC ACID $CH_3(CH_2)_{18}COOH$ is found partly free and partly as a glyceride in earth-nut oil (from *Arachis hypogœa* (Linn.)); in butter, and in the fruit of *Nephelium lappaceum* (Heintz. Pogg. 90, 146; Grössmann, Annalen, 89, 1; Oudemans, Zeits. f. Chem. 1867, 256). It has been prepared by treating behenolic acid $C_{22}H_{40}O_2$ with fuming nitric acid (Grössmann, Ber. 1893, 644), and synthetically from acetoacetic ester and octodecyl iodide (Schweizer, Arch. Pharm. 1884, 753); m.p. 77° (Baczewski, Monatsh. 17, 530).

ARACHIS OIL is obtained from the seeds of *Arachis hypogœa* (Linn.), which are known in commerce as earth nuts or monkey nuts. The cultivation of the arachis plant dates back so far in history that its origin is unknown. It is frequently assumed that the home of the arachis nut is Brazil. The plant is chiefly cultivated in the East Indies, Indo-China, Java, Japan, the West Coast of Africa, Mozambique, Madagascar, Egypt, Spain, Sicily, the United States of America, the Argentine, and in the West Indian Islands. The East Indian and West African nuts represent two distinct varieties. In commerce a distinction is made between decorticated and non-decorticated nuts. The Indian and Mozambique nuts are usually decorticated before they are shipped to Europe; as they undergo some detrimental changes on the voyage, they cannot be used for the production of best edible oil, and are mostly worked up for soap oil. The nuts coming from West Africa mostly arrive non-decorticated, and are therefore suitable for the preparation of best edible oil, the lower qualities only, derived from a second and third expression (*see* below) being used for technical purposes. The approximate composition of arachis nut, taking the average of nuts from various places of origin, is as follows: oil, 38–50 p.c.; water, 4·6–12·8 p.c.; albuminoids, 26–31 p.c.; carbohydrates, 5–19 p.c.; fibre, 1·1–4·1 p.c.; ash, 1·6–3·0 p.c.

The undecorticated nuts are shelled by special machinery and the inner red skin which surrounds the kernel is removed as completely as possible by a blast of air. The separated and cleaned kernels are then ground in the usual manner and subjected to hydraulic pressure. As the kernels contain so high a proportion of oil, the expression of the oil is carried out in two stages; frequently the meal is even expressed three times. The first expression takes place at the ordinary temperature, and yields the 'cold-drawn' oil; the second expression is carried out at a temperature of 30°–32°; and the third expression at 50°–55°.

The 'cold-drawn' oil is nearly colourless, and has a pleasant taste, recalling that of kidney beans; it is used as salad oil, and sold under the name 'huile surfine.' The oil obtained by the next expression also serves for edible purposes, in the sardine and margarine industries, or for burning; the lowest quality, which has been expressed at the highest temperature, is chiefly used for soap-making.

The arachis cakes serve as an excellent cattle food, for they contain the highest amount of proteids of all known oil cakes; moreover, these proteids are more easily digested than those of other cakes.

On standing a few degrees above freezing-point, 'stearine' deposits from arachis oil. This stearine contains *arachin* which does not settle out as a crystalline mass, so that it cannot be removed in the usual manner by expression. Hence it is necessary, in order to 'demargarinate' arachis oil, to allow it to stand for a prolonged time in the cold, when 'margarine d'arachide' settles out, so that the supernatant clear oil can be drawn off.

Amongst the solid fatty acids of arachis oil, arachidic acid and lignoceric acid have been identified. These two acids are characteristic of arachis oil, and as their proportion can be determined quantitatively, the separation and determination of 'crude arachidic acid' (*i.e.* a mixture of arachidic and lignoceric acids) furnishes an excellent means of identifying arachis oil, and determining its proportion in mixtures with other oils. Amongst the liquid fatty acids of arachis oil, oleic acid undoubtedly predominates; in addition to it there has also been proved the presence of hypogæic and linolic acids.

Arachis oil has a sp.gr. 0·917–0·919 at 15°; its iodine value fluctuates between 87 and 100. As the iodine value of arachis oil lies so near that of olive oil, adulteration of olive oil with arachis oil takes place on the largest scale; indeed, very frequently arachis oil is entirely substituted for olive oil (as in the preparation of tinned sardines).

Arachis oil is chiefly expressed in the South of Europe (Marseilles and Trieste); therefore the lower qualities of this oil enter largely into the composition of the soaps of South Europe. Thus, one of the most characteristic components of the Marseilles white soap is arachis oil. The quantity of arachis nuts imported into France during the year 1907 was: arachis nuts in shells, 163,241 tons; decorticated arachis nuts, 117,404 tons. The total quantity of arachis nuts produced in the world may be taken to amount to about 350,000 tons. Next to France, arachis nuts are largely imported into Trieste, Delft, and in smaller quantities to Germany (about 25,000 tons), and to the United States of America. The latter country produces about 50,000 tons per annum. J. L.

ARAGONITE. The orthorhombic form of calcium carbonate ($CaCO_3$), differing from the more common dimorphous form calcite (*q.v.*) in its greater density (sp.gr. 2·93), greater hardness (H. 3½), and in the absence of cleavage. It crystallises, together with calcite, from aqueous solutions containing carbon dioxide at temperatures above 18°, and the presence of various salts in the solution favours its growth. In nature it is deposited by thermal springs, for instance, those of Carlsbad in Bohemia, in the form of

pea-like concretions, this variety of the mineral being known as *pisolite*. Another variety, called *flos-ferri* (flower of iron), is found as snow-white coralloidal forms in the iron-mines of Styria. Crystals were first found embedded in red clay and gypsum in Aragon, Spain; and divergent groups of spear-like crystals have been found in an iron (hæmatite) mine in west Cumberland. L. J. S.

ARALIA BARK or *False Prickly Ash Bark*, the bark of *Aralia spinosa* (Linn.), contains a volatile oil, an amorphous bitter substance, (tannin), a grey acrid resin, and a glucoside to which the name *araleïn* has been given (Lilly, Pharm. J. [3] 13, 305). By boiling araleïn with dilute hydrochloric acid, *araliretin* is obtained (Holden, Pharm. J. [3] 11, 210; Chem. Soc. Trans. 40, 105).

ARAROBA POWDER. *Goa Powder*; *Chrysarobin.* A powder varying in colour from a pale primrose yellow to bronze and purple, which collects, possibly as the result of oxidation of the resin, in the cavities of the stems and branches of the *Andira Araroba* (Aguiar) (ord. *Leguminosæ*), a tree inhabiting the forests of Bahia in Brazil (Aguiar, Pharm. J. [3] 10, 42; *cf.* Greenish, *ibid.* [3] 10, 814).

Crude araroba was examined by Attfield in 1875 (Pharm. J. [3] 5, 721), and found to contain *moisture*, 1 p.c.; *glucoside, bitter constituent* and *arabin*, 7 p.c.; *yellow crystalline substance* extracted with benzol, supposed to be chrysophanic acid, 80–84 p.c.; *resins*, 2 p.c.; *woody fibre*, 5·5 p.c. On incineration, 0·5 p.c. of *ash* was obtained.

The yellow crystalline compound which constitutes the chief part of Goa powder and to which its activity is probably due, was subsequently examined by Liebermann and Seidler (Ber. 11, 1603; Annalen, 212, 29). It was shown to be *chrysarobin*, independent of, but closely related to, chrysophanic acid, and into which it is readily converted by the oxidising action of the air. This is most expeditiously effected by leading a current of air through Goa powder dissolved in aqueous potash. Hesse (Annalen, 309, 32) finds that araroba powder contains no chrysophanic acid, but is a mixture of chrysarobin $C_{15}H_{12}O_3$, with a substance yielding methyl iodide by Zeisel's method, which was assumed by Hesse to be chrysarobin methyl ether.

Araroba powder has been fully investigated by Jowett and Potter (Chem. Soc. Trans. 81, 1575), who have isolated the following substances: *chrysarobin* $C_{15}H_{12}O_3$; *dichrysarobin* $C_{30}H_{24}O_7$; *dichrysarobin methyl ether* $C_{31}H_{26}O_7$, melting at 160°; and a substance, $C_{17}H_{14}O_4$, m.p. 181°.

Pure chrysarobin prepared from the commercial product by extraction with light petroleum, distilling, and recrystallising the residue repeatedly from a large quantity of ethyl acetate, consists of lemon-yellow scales melting at 202° (corr.) insoluble in aqueous sodium carbonate, but soluble in caustic alkalis, giving a yellow solution which becomes red in the air. It dissolves in concentrated sulphuric acid with a yellow colour. On distillation with zinc, β-methyl anthracene is obtained. When acetylated, chrysarobin yields a diacetyl compound, $C_{15}H_{10}O_3Ac_2$, m.p. 193°, and a triacetyl compound, $C_{15}H_9O_3Ac_3$, m.p. 238°. A minute quantity (1 mg.) of chrysarobin sprinkled on a drop of fuming nitric acid gives a red solution, which when spread in a thin layer and treated with ammonia strikes a violet colour (Pharm, Germ.).

Dichrysarobin consists of orange crystals, decomposing at about 250°. It is distinguished from chrysarobin by being insoluble in benzene; it also appears to be more readily oxidised, yielding, similar to chrysarobin, chrysophanic acid. A hexa-acetyl derivative, $C_{30}H_{18}O_7Ac_6$, m.p. 178°-181°, has been obtained, and on distillation with zinc-dust β-methyl anthracene is formed.

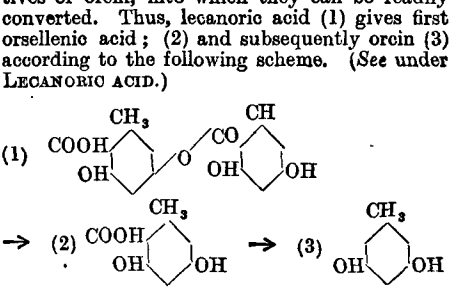
Though sometimes administered internally as a purgative, araroba powder is used in medicine almost exclusively as an external remedy in the form of ointment, in the treatment if certain skin diseases. A. S.

ARASINA GURGI. An impure gamboge from Camara, obtained probably from a species of Garcinia (Dymock, Pharm. J. [3] 7, 451).

ARBOL-A-BREA RESIN is obtained from *Canarium luzonicum* (Miq.), a tree belonging to the Burseraceæ, growing in the Philippines. The resin is greyish-yellow, soft, glutinous, and has a strong agreeable odour. It contains 61·29 parts of resin very soluble in alcohol; 25·00 parts of resin sparingly soluble in alcohol; 6·25 essential oil; 0·52 free acid; 0·52 bitter extractive matter; 6·42 woody and earthy impurities (Bonastre, Jour. Pharm. 10, 129). Baup has isolated four crystalline substances, *Amyrin*, *Breïdin*, *Breïn*, and *Bryoïdine* (Ann. Chim. Phys. [3] 31, 108).

ARBUTIN *v.* GLUCOSIDES.

ARCHIL or **ORCHIL** (*Orseille*, Fr.; *Orseille*, Ger.; *Oricello*, It.) appears in commerce in three forms: (1) as a pasty matter called *archil*; (2) as a mass of a drier character, named *persis*; and (3) as a reddish powder called *cudbear*. It is obtained from various lichens of the genus Roccella, growing on the rocky coasts of the Azores, the Canaries and Cape de Verd Isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, &c., and from *Ochrolechia tartarea*, growing in Sweden and Norway. None of these lichens contains the colouring matters ready formed, but they contain certain colourless acids of the type of *lecanoric acid*, derivatives of orcin, into which they can be readily converted. Thus, lecanoric acid (1) gives first orsellenic acid; (2) and subsequently orcin (3) according to the following scheme. (*See* under LECANORIC ACID.)



Orcin itself, when acted upon by air and ammonia, changes into a purple substance called *orcein*, which is the name applied to the colouring matters of archil (Robiquet, Ann. Chim. Phys. [2] 47, 238).

Finely powdered orcin is placed in a thin layer under a bell jar, together with a beaker containing strong ammonia solution. As soon

as the substance has become brown-coloured, it is removed and exposed to air for some time. It is then dissolved in very dilute ammonia solution, reprecipitated with acetic acid, and dried. According to Gerhardt and Laurent, orcin has the composition $C_{14}H_7NO_6$ (Ann. Chim. Phys. [3] 24, 315), but more recent researches indicate that it is a mixture of substances. Liebermann, for instance (Ber. 7, 247 ; 8, 1649), considers that by this reaction three colouring matters are produced, having respectively the formulæ (*a*) $C_{14}H_{13}NO_4$; (*b*) $C_{14}H_{12}N_2O_3$; and (*c*) $C_{14}H_{12}N_2O_2$.

Zulkowski and Peters (Monatsh, 11, 227) allowed orcin to remain in contact with ammonia for two months, and from the product isolated three substances:

(*a*) *Red orcein* $C_{28}H_{24}N_2O_7$, the main product, which appears to be formed according to the following equation :—

$$4C_7H_8O_2+2NH_3+6O=C_{28}H_{24}N_2O_7+7H_2O.$$

It is a brown crystalline powder, soluble in alcohol with a red colour, and in alkaline solutions with a blue-violet tint.

(*b*) A crystalline yellow compound, $C_{21}H_{19}NO_5$, which is accounted for as follows :—

$$3C_7H_8O_2+NH_3+3O=C_{21}H_{19}NO_5+4H_2O.$$

(*c*) An amorphous product similar to litmus.

These substances can be prepared much more rapidly by the addition of hydrogen peroxide to an ammoniacal solution of orcin.

There can be no doubt that this reaction proceeds in several stages, and that the character of the product varies according to the duration of the process. This is well known to manufacturers, who can prepare at will a blue or a red orchil. The constitution of these colouring matters has not yet been determined, but in view of the circumstances by which they are produced, it is most probable that they are members either of the *oxazine* or *oxazone* groups.

Orchil was originally prepared from the lichens by means of stale urine, which supplied the necessary ammonia, but ammonia solution is now exclusively employed. The older methods have, however, been greatly improved, and in the place of barrels the operation is carried out in large horizontal or vertical cylinders fitted with stirrers, and suitable openings for the admission of air.

In such an apparatus the weed is digested with about three times its weight of ammonia solution at 60° for from three days to one week, the admission of air being regulated according to the judgment of the manufacturer. The first product of the reaction has a blue colour, and if the process be stopped at this point, there is formed the dyeware known as *blue orchil*. On the other hand, if the action of the air and ammonia is allowed to proceed further, *red orchil* is obtained. These orchil pastes when dried and finely ground, constitute the product known as *cudbear*.

Bedford (Ger. Pat. 57612, 1889) blows air or oxygen through the ammoniacal mixture, which, especially in the latter case, materially shortens the process. The apparatus employed is erected vertically, and by an ingenious arrangement of projecting shelves, the edges of which are turned down, a considerable quantity of the air or oxygen is entrapped, and exerts therefore a more powerful oxidising effect.

Orchil liquor is prepared by extracting the lichens with boiling water, concentrating the extract to from 8 to 10°Tw., and submitting this to the action of air and ammonia; whereas *orchil extract* is produced by the extraction of orchil paste itself.

In former times archil and cudbear were frequently adulterated with magenta, certain azo-colours, extracts of logwood, brazilwood, &c.; but as the importance of these dyestuffs has now very greatly diminished, such a contamination is at the present time of rare occurrence.

Archil and its preparations are substantive colouring matters, which dye well in a neutral bath, but have the useful property of behaving nearly as well under slightly acid or slightly alkaline conditions. Even colours of considerable intensity are produced from it without difficulty, but unfortunately these are not fast to light. Wool is dyed in a neutral bath, or with addition of a trace of sulphuric acid, and silk is dyed in the presence of soap solution, acetic acid being sometimes added. Archil is not applied to cotton.

Archil was at one time employed to a large extent for 'bottoming' indigo, that is to say, the fabric was first dyed with archil and subsequently with indigo. The reverse process, known as 'topping,' has again been considerably in vogue. Cudbear and archil are also used to a limited extent in conjunction with other dyestuffs for the production of compound shades. White wines are sometimes coloured with archil, but its presence can be detected by precipitating with lead acetate and extracting with amyl alcohol, when a red colour indicates the presence of archil or magenta. The addition of a little hydrochloric acid changes the colour to yellow if magenta be present, but does not alter it if archil is the adulterant (Haas, Zeitsch. anal. Chem. 20, 869 ; J. Soc. Chem. Ind. 1, 119).

A. G. P.

ARCHIL REDS *v.* AZO- COLOURING MATTERS.

ARCHIL SUBSTITUTES *v.* AZO- COLOURING MATTERS.

ARECA. A genus of palms containing the important species *Areca Catechu* (Linn.) (*betel nut* or *areca nut*), the fruit of which is used as a masticatory in the East Indies. It contains an inferior catechu, tannic and gallic acids, ammonium acetate, fats, oils, gum, nitrogenous substances, and a dye (*areca red*). The charcoal of the nut is used as a tooth powder, and the ground nut is employed as a remedy for tapeworm.

AREOMETER *v.* HYDROMETER.

ARGAL *v.* ARGOL.

ARGAN OIL. An oil obtained from the kernels of *Argania Sideroxylon* (Roem. et Schult) (ord. *Sapotaceæ*), growing in Morocco. The kernels are first roasted, ground to powder and mixed with water, when the oil separates (Pharm. J. [3] 10, 127).

ARGENTAN. *Aluminium bronze* (*v.* ALUMINIUM).

ARGENTINE. A name given by R. Kirwan in 1794 to a variety of calcite ($CaCO_3$) occurring as small scales with a pearly white or silvery lustre.

ARGENTINE. Finely divided spongy tin,

made by reducing a weak solution of tin salt (120 grams in 60 litres of water) by zinc. The tin is collected in a sieve, washed with water, and dried at a gentle heat. Used for tin-plating and also for printing upon fabrics and paper (Deut. Ind. Zeit. 23, 255; J. Soc. Chem. Ind. 7, 504).

ARGENTITE. A mineral consisting of silver sulphide Ag_2S, and occurring as cubic crystals or as compact masses. It is blackish lead-grey in colour, and perfectly sectile; surfaces cut with a knife are bright and shining. Containing 87·1 p.c. of silver, it is a valuable ore of the metal when met with in quantity, as in the Comstock lode in Nevada and in Mexico.

L. J. S.

ARGENTOL. A synthetic antiseptic, consisting of a compound of silver, with quinosol, of the formula $C_9H_5N(OH)SO_3{\cdot}Ag$. Forms a yellowish powder, of a faint smell, sparingly soluble in water and alcohol (Pharm. Zeit. 1897, 42, 243).

ARGENTORAT. Trade name for a flash-powder consisting of a mixture of potassium perchlorate and aluminium, used in photography: gives very little smoke (*v.* FLASH-POWDERS).

ARGINASE. An enzyme occurring in the liver, also present in the kidney, the intestinal mucous membrane, thymus, and other organs (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 321), and found by Shiga (Zeitsch. physiol. Chem. 1904, 42, 502) among the enzymes obtained from yeast; it can be extracted from the liver by water or dilute acetic acid, and is precipitated from solution by alcohol, ether, or ammonium sulphate. Arginase is a specific enzyme for the exclusive hydrolysis of *d*-arginine or of substances containing the *d*-arginine grouping, which it converts almost quantitatively into carbamide and *d*-ornithine. Creatine and other guanidine derivatives structurally similar to arginine, or guanidine itself, are incapable of hydrolysis by this enzyme (Dakin, J. Biol. Chem. 1907, 3, 435).

M. A. W.

ARGININE $C_6H_{14}O_2N_4$, *α-amino-δ-guanino-n-valeric acid* $NH:C(NH_2){\cdot}NH{\cdot}(CH_2)_3{\cdot}CH(NH_2){\cdot}CO_2H$, first isolated by Schulze and Steiger (Ber. 1886, 19, 1177) from the etiolated germinated cotyledons of *Lupinus*, is the most widely distributed dissociation product of proteid matter, and can be obtained by hydrolysis of the proteid matter of seeds of *Lupinus luteus*, *Cucurbita pepo*, *Picea excelsa*, to the extent of 10 p.c., *Abies pectinata*, *Pinus sylvestris*, and other conifers (Schulze, Ber. 1891, 24, 276; Zeitsch. physiol. Chem. 1896, 22, 411, 435; 1897, 24, 276). According to Suzuki (Chem. Zeit. 1899, 23, 658) the arginine obtained from the seeds of conifers exists already formed, but in loose combination with the proteid material, and is also produced synthetically in the plant from ammonium salts and nitrates, either in full or diffused daylight (Bull. Coll. Agr. Tokyo Imp. Univ. 1900, 4, 25). Arginine is also one of the constituents of the product of hydrolysis of proteids of animal origin, thus, horn yields 2·25 p.c.; glue, 2·60 p.c.; conglutin, 2·75 p.c.; albumen from yolk of egg, 2·3 p.c.; from white of egg, 0·8 p.c.; blood serum, 0·7 p.c.; and casein, 0·25 p.c. (Hedin, Zeitsch. physiol. Chem. 1894, 20, 186), whilst the protamines *salmine*, *sturine*, *Clupeine*, *Scombrine*, *Cyclopterine*, and *Crenilabrine* yield arginine as the chief product of hydrolysis (Kossel, Zeitsch. physiol. Chem. 1896, 22, 176; 1898, 25, 165; 1899, 26, 588; 1904, 40, 565; 1910, 69, 138). In cases of phosphorus-poisoning arginine is found in the urine (Wohlgemuth, Zeitsch. physiol. Chem. 1905, 44, 74), whilst the amount obtained from the liver is diminished (Wakeman, Zeitsch. physiol. Chem. 1908, 44, 335).

When arginine is heated with barium hydroxide, it is decomposed into ammonia, carbamide, and ornithine (*q.v.*) (*αδ-diaminovaleric acid*); cyanamide reacts with ornithine at the ordinary temperature to form arginine (Schulze and Winterstein, Zeitsch. physiol. Chem. 1898, 26, 1; Ber. 1899, 32, 3191), or with *α*-benzoylornithine to form the benzoyl derivative of arginine, and this is readily hydrolysed to arginine, which is thus proved to be *α-amino-δ-guanino-n-valeric acid* (Sörensen, Ber. 1910, 43, 643).

Arginine crystallises in brilliant monoclinic plates (Haushofer, Zeitsch. physiol. Chem. 1887, 11, 53); m.p. 207°–207·5° (Gulewitz, Zeitsch. physiol. Chem. 1899, 27, 178); it also crystallises with $1H_2O$ in rhombohedra (Hedin, Zeitsch. physiol. Chem. 1895, 21, 160); it dissolves readily in water, and is sparingly soluble in alcohol. Arginine contains an asymmetric carbon atom, and the dextrorotatory form is the natural product, the hydrochloride has $[\alpha]_D+12{\cdot}5°$ in aqueous or $+25{\cdot}5°$ in hydrochloric acid solution. Arginine is strongly alkaline, and its solution absorbs carbon dioxide from the air; it forms well defined crystalline salts with acids, and compounds with certain metallic salts (Gulewitz, *l.c.*). The *nitrate* $C_6H_{14}O_2N_4$, $HNO_3,\frac{1}{2}H_2O$ has m.p. 126°; the *dinitrate* $C_6H_{14}O_2N_4,2HNO_3$ has m.p. 151°; the *hydrochloride* $C_6H_{14}O_2N_4,HCl,H_2O$ melts and decomposes at 209° when anhydrous; the *silver nitrate compounds* $C_6H_{14}O_2N_4,AgNO_3,\frac{1}{2}H_2O$ decomposes at 164°, and $C_6H_{14}O_2N_4,AgNO_3$, HNO_3 melts and decomposes at 180°; the *cupric nitrate compound* $2C_6H_{14}O_2N_4,Cu(NO_3)_2$, $3H_2O$ melts at 112°–114° or decomposes at 232°–234° when anhydrous; the *copper sulphate compound* melts at 110° or decomposes when anhydrous at 235°–238°; the *picrate* $C_6H_{14}O_2N_4$, $C_6H_3O_7N_3,2H_2O$, m.p. 205°, dissolves in 204·1 parts of water at 16°; the *picrolonate* $C_6H_{14}O_2N_4$, $C_{10}H_8O_5N_4,H_2O$, m.p. 231°, dissolves in 1124 parts of water, or 2885 parts of alcohol at the ordinary temperature (Schulze and Steiger, Ber. 1886, 19, 1177; Hedin, Zeitsch. physiol. Chem. 1894, 20, 186; Gulewitz, *ibid.* 1899, 27, 178; Steudel, *ibid.* 1903, 37, 219; Reisser, *ibid.* 1906, 49, 210).

Certain acyl derivatives and esters of arginine have also been prepared, the *dibenzoyl derivative* $C_6H_{12}O_2N_4Bz_2$ crystallises in rhombic needles or prisms, m.p. 217·5°–218° (Gulewitz, *l.c.*), the *β-naphthalenesulphonic derivative* $C_6H_{13}O_2N_4{\cdot}SO_2{\cdot}C_{10}H_7$ is a colourless powder, m.p. 88°–89° (Reisser, *l.c.*); *diarginylarginine* is isolated as the *dipicrate* $C_{18}H_{28}O_4N_{12}(C_6H_3O_7N_3)_2,2H_2O$, m.p. 207°, from the product obtained by hydrolysing pepsin extract with hydrogen fluoride;

arginylarginine picrate $C_{12}H_{26}O_3N_8,C_6H_3O_7N_3,2H_2O$, m.p. 213°, is similarly obtained from gelatin (Hugouenq and Morel, Compt. rend. 1909, 148, 236); *arginine methyl ester hydrochloride* has m.p. 195° (corr.) with decomposition, the *picrate* forms lemon-yellow crystals, which melt and decompose at 218° (corr.); and the *nitrate* melts at 189° (corr.) (Fischer and Suzuki, Sitzungber. K. Akad. Wiss. Berlin, 1904, 1333).

The presence of arginine assists the tryptic digestion of proteid matter and aids the emulsification of fats: this appears to be connected with its alkalinity, as sodium carbonate acts similarly (Lawroff, Zeitsch. physiol. Chem. 1899, 28, 303). When arginine (hydrochloride or carbonate) is administered as a food, it suffers complete decomposition, and 37–77 p.c. of the nitrogen so given reappears as urea (Thompson, Zeitsch. physiol. Chem. 1905, 33, 106), and the amount of arginine in the various organs shows no increase (Orglmeister, Beitr. Chem. Physiol. Path. 1905, 7, 27).

Arginine is readily oxidised by hot calcium or barium permanganate yielding guanidine, γ-guaninobutyric acid and succinic acid (Bénech, Kutscher, Zeitsch. physiol. Chem. 1901, 32, 278, 413), and the estimation of the number of arginine groups in proteids is based on this reaction (Orglmeister, *l.c.*; Kutscher and Zickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, 28, 624), the guanidine thus obtained being isolated in the form of its sparingly soluble picrate, and either weighed as such, or the nitrogen estimated in the usual way. Another method of isolating and estimating arginine is based on Siegfried's carbamino-reaction of amino-acids (Zeitsch. physiol. Chem. 1905, 44, 85; 46, 402; 1907, 50, 171; Ber. 1906, 39, 397), whereby the barium, strontium, or calcium salt of the corresponding carbamic acid is formed when carbon dioxide is passed into a solution of the amino-acid containing excess of alkali earth hydroxide until the solution is neutra to phenolphthaleïn—

$$\begin{matrix}R{\cdot}CH{\cdot}NH_2\\ |\\ CO_2H\end{matrix} + Ca(OH)_2 + CO_2 = \begin{matrix}R{\cdot}CH{\cdot}NH{\cdot}CO_2\\ |\\ CO_2\end{matrix}\!\!>\!Ca + H_2O.$$

The barium and strontium salts of these complex carbamic acids are much less readily soluble than the corresponding amino-acid, and afford a means of isolating the compounds (D. R. P. 188005, 1906). In order to estimate the amino-acid, the filtrate containing the calcium salt of the carbamic acid is decomposed by heating with boiled-out water into calcium carbonate, and the amino acid; the ratio $CO_2:N$ is determined by weighing the calcium carbonate thus precipitated, and estimating the nitrogen in the filtrate by Kjeldahl's method (Zeitsch. physiol. Chem. 1908, 54, 423).

dl-Arginine is readily produced by the tryptic fermentation of fibrin, or by heating *d*-arginine nitrate at 210°–220° for 15–20 minutes (Kutscher, Zeitsch. physiol. Chem. 1901, 32, 476) or by heating *d*-arginine in 50 p.c. sulphuric acid in sealed tubes at 160°–180° for 33 hours (Reisser, Zeitsch. physiol. Chem. 1906, 49, 210); it decomposes at 210° (Cathcart, Proc. Physiol. Soc. 1905, 39); the *nitrate* $C_6H_{14}O_2N_4,HNO_3$, has m.p. 216°; the *dinitrate* $C_6H_{14}O_2N_4,2HNO_3$, m.p. 151°; the *cupric nitrate derivative* $2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O$, m.p. 228°–229°; the *silver nitrate derivative* $(C_6H_{14}O_2N_4,HNO_3)_2,AgNO_3$, m.p. 170°–172°; the *picrate* $C_6H_{14}O_2N_4,C_6H_3O_7N_3$, m.p. 200°–201°, is sparingly soluble 100 parts of water at 16° dissolve 0·22 parts; the *picrolonate* $C_6H_{14}O_2N_4,C_{10}H_8O_5N_4$, m.p. 248°, 100 c.c. of water at 16° dissolve 0·03 grams of salt; the *β-naphthalene sulphonate* $C_6H_{12}O_2N_4\cdot SO_2\cdot C_{10}H_7,\frac{1}{2}H_2O$, has m.p. 85°–90° (Reisser, *l.c.*).

l-Arginine is formed by treating *dl*-arginine carbonate with the expressed juice of calf's liver, the ferment *arginase* present in the extract destroys the *d*-arginine, and does not attack the lævo- isomeride. With the exception of the difference in optical activity, the salts of *l*-arginine are identical with those of the dextro-isomeride, *l-arginine hydrochloride* has $[\alpha]_D^{20°}$ −20·51° (Reisser, *l.c.*). M. A. W.

ARGININE. This name has also been given to an alkaloid discovered by Quiroga (J. Pharm. Chim. 1896, 16, 293) in a species of laurel (known by the natives as *viraro-mi*), growing in the east of the Argentine and west of Brazil. It forms prismatic crystals, soluble in chloroform or benzene, slightly soluble in ether, petroleum spirit, or water. Its aqueous solutions, acidified with hydrochloric acid, give a white ppt. with bromine water and a white ppt. with alkali soluble in excess. The bark and cambium contain 1·5–1·6 p.c., the wood 0·04–0·05 p.c. of the alkaloid. H. I.

ARGOL or **ARGAL.** (*Tartre brut*, Fr.; *Weinstein*, Ger.) Crude potassium bitartrate, known as red argol (*Cremore di Vinaccia*), or white argol (*Cremore di St. Artimo*), according to whether it is deposited from the red or the white grape (*v.* TARTARIC ACID).

ARGON. Sym. A or Ar. At. wt. and molec. wt. 39·88. As long ago as 1785, Cavendish (Phil. Trans. 75, 372) made experiments in order to determine whether the inert residue left after withdrawing oxygen, water, and carbon dioxide from air was homogeneous. He sparked a mixture of air and oxygen in presence of potash for the absorption of the acid produced, and removed the excess of oxygen by a solution of liver of sulphur. Only a small bubble of gas remained unabsorbed, and this did not diminish in volume on further sparking with oxygen. Cavendish concluded 'that if there is any part of the' nitrogen 'of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.'

Cavendish's work was overlooked for more than a century, and attention was only directed to it after the discovery, in 1894, by Lord Rayleigh (Roy. Soc. Proc. 55, 340), that the density of 'atmospheric nitrogen' was one-half per cent. higher than that of nitrogen prepared by chemical means. This result gave fresh indication of the existence of some hitherto undiscovered gas in the atmosphere, and further

investigations, carried out jointly by Rayleigh and Ramsay (Phil. Trans. 186, 187), led to the isolation of a new gaseous element. The gas, which has a density of approximately 20, and which constitutes nearly 1 p.c. by volume of the atmosphere, was called *argon*, owing to its remarkable chemical inertness, in virtue of which it can be readily separated from the accompanying nitrogen.

Argon occurs in the atmosphere to the extent of 1·3 p.c. by weight (Leduc, Compt. rend. 123, 805) and 0·933 p.c. by volume (Schloesing, Compt. rend. 121, 604; Moissan, Compt. rend. 137, 600). It also occurs in a large number of mineral waters and thermal springs (Bouchard, Compt. rend. 121, 392; Troost and Ouvrard, *ibid.* 121, 798; Moissan, *ibid.* 135, 1278; Moureu, *ibid.* 135, 1335; 142, 1155), and in the volcanic gases of Mt. Pelée (Moissan, Compt. rend. 135, 1085); it is found, moreover, in fire damp and in coal (Schloesing, Compt. rend. 123, 233). Argon has also been observed, together with helium, in the gas evolved on heating numerous minerals.

Preparation.—(i.) *By sparking air with oxygen*, the method originally employed by Cavendish (*v. supra*). The gas is preferably confined over mercury, and a small quantity of potash introduced through a curved pipette. The sparks are passed between the ends of stout platinum wires, fused through the ends of U-shaped glass tubes. These tubes are filled with mercury, and serve to establish electrical connection with the secondary terminals of a Ruhmkorff coil capable of giving a 6-inch spark through air when worked by four lead accumulators. The sparking is usually continued for several hours after contraction has ceased; the excess of oxygen is then absorbed by phosphorus (Rayleigh and Ramsay, *l.c.*; Rayleigh, Chem. Soc. Proc. 13, 181; Becker, Z. Elek. 9, 600). To save time, it is customary to prepare by method (ii.) a gas consisting mainly of argon, and to employ the method of sparking only to remove the last traces of active gases.

(ii.) *From 'atmospheric nitrogen,' the nitrogen being absorbed by a metal.* In their original investigation, Rayleigh and Ramsay separated argon from nitrogen by continuously circulating the mixture over red-hot magnesium shavings, whereby the nitrogen was absorbed, forming magnesium nitride (*cf.* Ramsay and Travers, Roy. Soc. Proc. 64, 183). This method is no longer used; a dry mixture of pure lime (5 parts) and magnesium dust (3 parts), introduced by Maquenne, is employed instead, which, when heated to redness, produces metallic calcium and absorbs nitrogen with great rapidity. By passing atmospheric nitrogen over this red-hot mixture, and leading the residual gas over metallic calcium heated to dull redness, complete absorption of the nitrogen is readily effected (Moissan and Rigaut, Compt. rend. 137, 773). Metallic lithium has also been employed for the same purpose (Guntz, Compt. rend. 120, 777; 123, 995).

(iii.) The readiest means of preparing argon in quantity consists in leading air slowly over a mixture of calcium carbide (90 p.c.) and calcium chloride (10 p.c.) heated to 800°, the mixture having previously been heated under diminished pressure to drive off any volatile matter. Both oxygen and nitrogen are absorbed by the mixture. The issuing gas is led over hot copper oxide to burn any hydrogen, hydrocarbons, and carbon monoxide present, and the water vapour and carbon dioxide removed. Using 7 kilos. of carbide, 11 litres of argon may be obtained in two days (Fisoher and Ringe, Ber. 41, 2017).

The gas prepared by the above methods contains traces of the other inert gases *neon*, *krypton*, and *xenon*, from which it is separated by fractional condensation and evaporation (Ramsay and Travers, Roy. Soc. Proc. 67, 329; Liveing and Dewar, Roy. Soc. Proc. 68, 389). The total quantity of these gases present is, however, only 0·25 p.c., and 85 p.c. of this impurity is neon.

Argon is a colourless gas, condensing to a colourless liquid, boiling at 86·9° abs. (−186·1°), at which temperature its density is 1·4046 (Baly and Donnan, Chem. Soc. Trans. 81, 914). Its m.p. is 83·4° abs. (−189·6°), its critical temperature is 155·6° abs. (−117·4°), and its critical pressure is 52·9 atmos. (Ramsay and Travers, Roy. Soc. Proc. 67, 329).

Argon is more soluble in water than nitrogen, the absorption coefficient being 0·02561, at 1°, and falling regularly to 0·02567 at 50° (Estreicher, Zeitsch. phys. Chem. 31, 176); these figures may, however, be in error by 5 p.c. (*v.* Fox, Chem. News, 99, 250). The refractive index of the gas for sodium light at N.T.P. is 1·0002837 (Burton, Roy. Soc. Proc. 1908, 80, 390); its thermal conductivity is 0·00003894 (Schwaize, Pogg. Ann. 11, (iv.) 303); and its molecular specific heat at constant volume is 2·977 cals. (Pier, Z. Elek. 15, 536). Its coefficient of expansion is 0·003668 (Kuenen and Randall, Roy. Soc. Proc. 59, 60). Argon passes through rubber more quickly than nitrogen (Rayleigh, Phil. Mag. 49, (v.) 220) or carbon dioxide (Kistiakowski, J. Russ. Chem. Soc. 30, 576), and does not pass through heated platinum or palladium; it is diamagnetic (Tanzler, Pogg. Ann. 24, (iv.) 931). (For its rate of effusion, *v.* Donnan (Phil. Mag. 49, (v.) 423).)

The density of argon has been determined by several observers, with the following results: (O=16); 19·940 (Rayleigh, Roy. Soc. Proc. 59, 201), 19·941 (Ramsay, Phil Trans. 186, 238); 19·945 (Fischer and Hahnel, Ber. 43, 1435). Argon is a member of the group of inert gases, and up to the present all attempts to combine it with other elements have failed (Rayleigh and Ramsay, *l.c.*; but *cf.* Cooke, Zeitsch. physikal. Chem. 55, 537).

Atomic and molecular weight. The molecular weight, 39·88, follows from the density determinations just cited; but the atomic weight cannot be determined in the usual manner, since argon forms no compounds with other elements. The ratio of the specific heat at constant pressure to the specific heat at constant volume is 1·644 (Rayleigh and Ramsay, *l.c.*), and this result, from analogy with the case of mercury vapour and by comparison with the ratio 1·666 theoretically required for a monatomic gas according to the kinetic theory, is regarded as proof that

argon is monatomic. Its atomic weight is therefore 39·88.

Spectrum. This is extremely characteristic, and has been carefully examined by Crookes (Phil. Trans. 186, 243), Kayser (Chem. News, 72, 99), Eder and Valenta (Monatsh. 16, 893; 17, 50), and by Trowbridge and Richards (Phil. Mag. 43, (5) 77). The most prominent lines are two in the red, having wave lengths of 6965·6 and 7056·4, a yellow line (6038·4), two green lines (5610 and 4702), and a violet line (4200).

ARGYRODITE. A sulpho-germaniate of silver, being the mineral in which the element *germanium* was discovered in 1886. It had, however, been mentioned by A. Breithaupt in 1823, under the name *Plusinglanz.* These occurrences in the Himmelsfürst silver-mine at Freiberg, Saxony, show only botryoidal crusts with a minutely crystallised surface. Later, the mineral was found as distinct, though small, cubic crystals in Bolivia, analysis of which proved the formula to be Ag_8GeS_6 (S. L. Penfield, 1893 and 1894). More recently, cubic crystals of larger size (3–5 cm. across) from Colquechaca, Bolivia, have been described and analysed (V. M. Goldschmidt, 1908). At this locality the mineral appears to be not uncommon, and no doubt large quantities of it have been smelted for silver. In external appearance it is not unlike argentite, but is less sectile than this.

In the Bolivian mineral the germanium may be replaced isomorphously by tin, giving the species *canfieldite* Ag_8SnS_6 (Penfield, 1894). Intermediate members of this series, or stanniferous argyrodite, also occur (Prior and Spencer, 1898). L. J. S.

ARIBINE *v.* VEGETO-ALKALOIDS.

ARICINE *v.* VEGETO-ALKALOIDS.

ARISTOCHIN. Trade name for di-quinine carbonate $CO(O{\cdot}C_{20}H_{23}N_2O)_2$.

ARISTOL. Dithymol di-iodide used as an iodoform substitute.

ARJUN WAX *v.* WAXES.

ARMENIAN BOLE *v.* PIGMENTS.

ARNATTO *v.* ANNATTO.

ARNICA *v.* RESINS.

ARNICA YELLOW *v.* AZO- COLOURING MATTERS.

ARNOTTO *v.* ANNATTO.

AROMATIC VINEGAR *v.* ACETIC ACID.

ARRACK. (*Arack* and *Rack*, Fr.; *Arrack*: *Reisbrauntwein*, Ger.) The term 'araq' or 'arak' was applied by the Arabs to distilled spirits generally, but it is now usually restricted to the spirituous liquor obtained by distillation of the fermented juice of the coco-nut palm (toddy or palm wine), or from rice, or from a mixture of both. Arrack is also made from the succulent flowers of the Bassia genus of trees and from other vegetable products, and is manufactured not only in the East, but also in the West Indies.

Where rice is used, it is steeped in water in large vats and agitated cautiously (so as not to damage the grains, which would interfere with the subsequent fermentation) until about half the rice has begun to germinate. The water is then run off from below, and toddy or molasses or a mixture of these is added to the rice. The whole is allowed to ferment, and the mixture is then distilled.

This method, which is said to produce the best quality of arrack, obtains at Batavia and in Jamaica, but in India arrack is frequently made from toddy alone.

The best qualities of arrack are agreeable to the taste and wholesome, which cannot be said of the commoner kind made from rice alone, in some parts of India and China. This has a somewhat nauseous odour and taste, due to a volatile oil which distils from the rice, and is narcotic and very unwholesome. Its intoxicating effect is frequently increased by the addition of hemp leaves, poppy heads, stramonium juice, &c.

A large amount of revenue is obtained from the manufacture of arrack in Siam and Ceylon, and the latter exports a considerable quantity to the United Kingdom, where it is used as a valuable ingredient in making *punch.*

An imitation arrack is sometimes made by flavouring rum with flowers of benjamin or benzoic acid. J. C.

ARROPE. Sherry boiled to a syrup used for colouring other wines.

ARROWROOT. The starch obtained from the rhizomes of *Maranta arundinacea*, grown in the West Indies. The starch prepared from other roots is often known locally as arrowroot; *e.g.* in Queensland, where the tubers of *Canna edulis* supply such a product.

The composition of the roots of true arrowroot grown in Jamaica is:

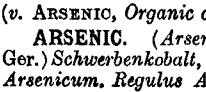
Water	Starch	Dextrin and sugar	Crude fibre	Ether extract	Proteid	Ash
63·4	27·8	2·1	3·9	0·2	1·6	0·9

(Leuscher, Zeit. öffentl. Chem. 1902, 8, 23.)

Commercial arrowroot contains from 83·5 to 86·9 p.c. starch, 11·0 to 15 p.c. water, proteins from 0·4 to 1·4 p.c., with small quantities (*circa* 0·3 p.c.) of ash, cellulose, and fat.

(For a series of analyses of arrowroots from various sources, *see* Ballard, Jour. Pharm. 1903, 17, [10] 476.) H. I.

ARSACETIN. The sodium salt of acetyl-*p*-aminophenyl arsenic acid—



(*v.* ARSENIC, *Organic compounds of*).

ARSENIC. (*Arsenic*, Fr.; *Arsenic, Arsen*, Ger.) *Schwerbenkobalt, Fliegengift, Näpfchenkobalt Arsenicum. Regulus Arsenici.* Symbol, As; at. wt. 74·96.

Occurrence.—Arsenic, in small quantities, is one of the most widely distributed elements; it is found in mineral and other waters, and in coal smoke, in most pyretic minerals, and in a large number of ores.

In England it occurs principally with *tin ore*, and on the Continent in *mispickel.* Arsenic occurs native (usually associated with iron, cobalt, nickel, antimony, and silver) in crystalline rocks and in the older schists, generally in reniform and stalactitic masses, often mammillated; it also occurs occasionally in rhombohedral crystals. At Zimeoff in Siberia, large

masses are found; it occurs in the silver-mines of Freiberg, Annaberg, Marienberg, and Schneeberg in Saxony; at Joachimsthal in Bohemia, Andreasberg in the Hartz, Kapnik in Transylvania, Orawitza in the Banat, Kongsberg in Norway, St. Marie-aux-Mines in Alsace, in Borneo, and in the United States.

As *arsenide* it occurs combined with iron in two forms $FeAs_2$ and Fe_2As_4; with nickel as *Kupfernickel* NiAs and $NiAs_2$; with cobalt as *tin white cobalt*, $CoAs_2$. With antimony it occurs as *arsenical antimony*, at Przibram in Bohemia; with blende, antimony and spathic iron, at Allemont, at Schladming in Styria and Andreasberg in the Hartz.

Arsenic is generally present in native sulphur. Combined with sulphur it occurs as *realgar* or *ruby sulphur* As_2S_2 in Hungary, Saxony, Switzerland, and China; and as *orpiment* As_2S_3 in Hungary and the Hartz.

With *sulphur* and *iron* it occurs as *mispickel, arsenical pyrites*, or *white mundic* FeS_2FeAs_2; with sulphur and cobalt in *cobalt glance* CoS_2CoAs_2; in *nickel glance* NiS_2NiAs_2, and in a number of other ores, being obtained as a secondary product in the roasting of *tin* and *copper ores, copper nickel, arsenical fahl ores, smaltine, cobalt* and *nickel glance*, &c.

With *oxygen*, arsenic occurs as *arsenolite* or *arsenite* As_4O_6, usually as a crust on other arsenical minerals, being formed by their decomposition. With *oxygen* and *cobalt*, it forms *cobalt bloom* or *arsenate of cobalt*; it also occurs as arsenates of iron, copper, and lead.

Preparation.—Metallic arsenic is used only to a small extent in commerce. It is usually prepared from native arsenic, arsenical iron, or mispickel, the latter being the only mineral used to any extent in England. The mineral used is heated in earthenware retorts or tubes laid horizontally in a long furnace. Great care is required in manufacturing the retorts; a mixture of 1 part fresh clay and 2 parts bricks or old retorts powdered, is made into the proper form, coated with a mixture of blood, loam, forge-scales and alum to produce the glaze, and burned. They are very strong and heat-resisting, and quite impervious to the vapour of arsenic. A piece of thin iron sheet is rolled and inserted into the mouth of the retort, and an earthen receiver luted on. On distilling, most of the arsenic condenses in the iron as a nearly white, coherent, internally crystalline mass, and is detached on cooling by unrolling the iron. If required, the arsenic is purified by redistillation.

At Altenberg in Silesia, arsenious oxide is heated with charcoal in an earthen crucible covered with an inverted crucible or conical iron cap. This method is more economical and productive than the one above described, but the metal is grey and pulverulent, and always contains arsenious acid.

It may also be prepared by heating the sulphides with charcoal and sodium carbonate or potassium cyanide.

Properties.—Arsenic is a very brittle steel-grey metalline mass of sp.gr. 5·62 to 5·96, of brilliant lustre, crystallising in rhombohedra, isomorphous with metallic antimony. It is a good conductor of electricity, and is odourless and tasteless.

It is volatile at temperatures above 100°, and is rapidly vaporised at a dull-red heat. At the ordinary pressure it volatilises without previous fusion, the vapour being yellow and of a garlic smell, but when heated under pressure it melts at 500° (Landolt). Joubert states that above 200° its vapour is phosphorescent (Compt. rend. 78, 1853).

When the vapour is condensed at a temperature but little below the volatilising point, *i.e.* when condensed in an atmosphere of arsenic, a nearly white compact mass of strongly metallic lustre is produced which scarcely oxidises in the air even when heated to 80°. When it is deposited on a colder surface or in an atmosphere other than arsenic, it forms less dense, dark-grey crystals which readily oxidise in the air even in the cold, and especially on heating.

Ludwig (Arch. Pharm. [2] 97, 23) has obtained arsenic (?) with a perfectly bright surface resembling freshly granulated zinc, and of the low density 5·395, by distilling in a tube with a small quantity of iodine.

When heated in air it absorbs oxygen, burning with a bluish flame and forming arsenious oxide. In pure water it is unaltered, but when exposed to air it forms a grey powder supposed by some to be a suboxide, but probably a mixture of metallic arsenic and arsenious oxide; this powder is sold as 'fly-powder.' When powdered and thrown into chlorine, it ignites, forming the trichloride; with the aid of heat it combines with bromine, iodine, and sulphur. Hydrochloric acid has but little action on arsenic, but it is rapidly dissolved by nitric acid, aqua regia, or by a mixture of hydrochloric acid and potassium chlorate.

When deflagrated with nitre it forms potassium arsenate.

Bettendorf (Annalen, 144, 110) has obtained a specular, amorphous, vitreous arsenic of sp.gr. 4·69–4·716 by subliming arsenic in a stream of hydrogen and condensing it at 210°–220°. At 360° it is converted into the crystalline form with the evolution of considerable heat, and when heated suddenly it hisses and gives off vapour whilst transforming.

Arsenic is a constituent of many alloys; it is used for bronzing brass and for the manufacture of opal glass.

(For the distribution of arsenic in commercial products, *v. Arsenious oxide.*)

Detection. — Arsenical compounds, when heated on charcoal, give off the characteristic garlic odour and white fumes of the oxide, with a white incrustation on the charcoal some distance from the assay. Metallic arsenic, and many arsenical minerals, such as mispickel, when heated in a tube closed at one end, form a blackish, shining metallic ring on the cooler portion of the tube; if heated in a tube open at both ends, the arsenic is oxidised, and condenses in a ring of white octahedral crystals, their shape being plainly visible under a lens. On cutting off the closed end of the tube containing the metallic mirror, and heating, it is also converted into the white ring higher up the tube. The white crystals dissolve in boiling

water, and the solution shows the usual tests for arsenic. Antimony under like circumstances would produce a white ring, which, however, is not crystalline, and is not soluble in water. Oxides of arsenic require to be mixed with charcoal before they produce the black mirror. Sulphides require the addition of alkaline carbonate or potassium cyanide, or they may be heated with baryta alone (Brame).

White arsenic when heated with about 3 parts of sodium acetate, gives the offensive smell of kakodyl.

In solution the reactions of the two series of compounds, the arsenious and the arsenic, differ considerably; generally speaking, arsenic compounds may be converted into the arsenious form by heating with sulphurous acid or with a sulphite.

Reinsch's test. If a piece of clean metallic copper is immersed in a solution of arsenious acid or an arsenious compound acidulated with pure hydrochloric acid, it is coated with a grey film, which is probably an arsenide of copper. The action proceeds better at the boiling temperature. The acid must first be tested in the same manner to ensure the absence of arsenic, which is always present in the commercial acid. The metal is washed, dried gently and heated in a tube, when the arsenic becomes oxidised and forms a *crystalline ring* on the colder part of the tube. A film due to antimony, as mentioned before, would not produce a crystalline ring.

This method is used in testing for and removing arsenic from hydrochloric acid, and in toxicology; by it 1 part of arsenic can be detected in 250,000 parts of solution.

It is not so delicate as Marsh's or the electrolytic method.

When hydrogen is generated in a liquid containing an arsenious compound, the arsenic combines with it and passes off as the gaseous hydride; many very delicate tests are based on this reaction.

(1) *Fleitmann's test.* The solution is mixed with excess of caustic potash, a piece of *pure* zinc, or of magnesium, or aluminium foil inserted, and the solution heated. A piece of filter paper moistened with silver nitrate is held over the mouth of the tube. In presence of arsenic, arseniuretted hydrogen is produced and reduces the silver on the paper forming a greyish or purplish colour. Antimony is not evolved in this test. Fleitmann's test is therefore a ready means of finding arsenic in presence of antimony; it is not, however, so delicate as Reinsch's, Marsh's, or the electrolytic method.

(2) *Marsh's test.* This or Reinsch's test is usually used in toxicology. The solution is acidulated with pure hydrochloric acid and introduced into an apparatus in which hydrogen is generated by means of pure sulphuric acid and zinc. Arsenic hydride is formed and is passed through a narrow glass tube, which is heated at one spot by a lamp; the arseniuretted hydrogen as it passes over the heated portion is decomposed with the precipitation of arsenic as a black ring. In testing for very small quantities of arsenic, the action should be continued for about an hour. A blank experiment should always be performed in the same manner to ensure the purity of the zinc and acid. It is essential not only to obtain zinc and acid which are free from traces of arsenic, but also to see that the zinc used is 'sensitive,' and will permit all the arsenic in the solution to be evolved as arseniuretted hydrogen. The presence in the solution of certain metals—notably iron—is liable to retard, or entirely prevent, the evolution of arseniuretted hydrogen. (On the presence of arsenic in glass as a source of error in the detection of arsenic, *v.* W. Fresenius, Zeitsch. anal. Chem. 22, 397; Ber. 17, 2938.) Instead of heating the tube, the gas may be ignited at the mouth of the tube, and the flame caused to impinge on a cold surface of porcelain, or preferably of platinum foil. The arsenic film may be distinguished from that produced by antimony as follows:—

(1) The arsenic film is quickly evaporated, while that of antimony only slowly disappears. Helling (Das Microscop in der Toxicologie) recommends that small spots be heated and the vapour received on a slip of glass, when, under the microscope, the octahedral crystals due to arsenic are visible.

(2) The arsenic film quickly dissolves in a solution of sodium hypochlorite; the antimony film is very slowly soluble.

(3) The antimony film dissolves quickly in yellow ammonium sulphide, leaving an orange-yellow residue on evaporation; the arsenic film dissolves very slowly.

Magnesium may also be employed in place of zinc, and E. Davy and Al. Jandousch use an amalgam of 1 part sodium in 8 parts mercury, with or without acid.

The presence of nitrates or nitric acid interferes with this test, and the acids used should be dilute.

(For the detection and estimation of arsenic by electrolytical methods, *v. Arsenic* in art. ANALYSIS, ELECTRO-CHEMICAL.)

Estimation.—Arsenic is usually estimated as (1) magnesium pyro-arsenate; (2) as arsenic sulphide; (3) as metallic arsenic.

(1) For this method it is necessary that the substance should be present as an *arsenic* compound. The conversion from the arsenious to the arsenic condition may be effected by heating with nitric acid (*v.* Estimation as sulphide) or hydrochloric acid and potassium chlorate.

The acid solution, which should occupy only a small bulk, is mixed with 'magnesia mixture' and rendered *strongly* alkaline with ammonia. After standing for 24 hours, the solution is filtered, the last portions of the precipitate, which consists of ammonium magnesium arsenate, being washed entirely on to the filter paper with a little of the filtrate (the volume of this filtrate should be noted roughly). The precipitate is then washed with a mixture of 1 part strong ammonia and 3 parts water, until only a slight opalescence is produced on the addition of nitric acid and silver nitrate to a few drops of the washings. It is then dried, detached as much as possible from the filter paper, and transferred to a weighed porcelain crucible, moistened with nitric acid, dried, and ignited, at first gently, and finally to bright redness. The

paper is moistened with nitric acid, dried, and ignited on the lid, and the crucible and its contents weighed. The ignited residue consists of magnesium pyro-arsenate $Mg_2As_2O_7$, and contains 48·27 p.c. of arsenic.

On account of the solubility of the ammonium magnesium arsenate, an addition should be made to the weight obtained of 0·001 gram for each 16 c.c. of filtrate obtained, not counting the washings.

(2) The arsenic for this method should be in the arsenious form. If *arsenic* compounds are present, they are preferably reduced by passing a current of sulphurous acid through the liquid, the excess of that gas being driven off by subsequent heating. Sulphuretted hydrogen is then passed through the liquid until thoroughly saturated, the liquid left to stand for some time, the excess of sulphuretted hydrogen driven off by heating, and the precipitated arsenious sulphide containing sulphur filtered off. The sulphide is dissolved in ammonia, filtered if necessary, and the arsenic estimated in the solution by one of the three following methods:—

(*a*) The solution is evaporated to dryness in a porcelain dish, then covered with an inverted funnel, and fuming nitric acid added. After the first violent action has ceased, the liquid is heated on a water-bath until the whole of the sulphur has disappeared, and only a small bulk of liquid remains; 'magnesia mixture' is then added, followed by excess of ammonia, and the process followed as already described.

(*b*) The ammoniacal solution is evaporated to dryness in a porcelain dish, and heated on a sand-bath to drive off the whole of the free sulphur and carbonise any organic matter (which is frequently present in toxicological analysis) without volatilising any of the arsenious sulphide. The residue is again dissolved in ammonia, filtered if necessary, evaporated to dryness, and gently heated in a weighed porcelain dish, and weighed as arsenious sulphide As_2S_3 (Mohr, Chem. Toxicologie, 56).

(*c*) The arsenic in the solution may be estimated by means of standard iodine solution (Champion and Pellet, Bull. Soc. chim. [2] 26, 541).

(3) For this method the arsenical mirror obtained by the Marsh-Berzelius method or the electrolytic method may be estimated by comparison with standard mirrors obtained under similar conditions to the estimation. Experience has shown that when in the preparation of standard mirrors, the quantities of arsenic used differ by amounts such as 0·002 milligram, a series of mirrors can be obtained showing differences in intensity which are sufficiently distinct and constant to be utilised for comparison.

Separation from other metals.—Certain heavy metals, if present, would be precipitated with the arsenious sulphide by means of sulphuretted hydrogen. From the sulphides of lead, bismuth, &c., the arsenious sulphide can be dissolved by digestion in ammonium sulphide. The solution would also contain antimony and tin, if present. The separation of arsenic from these two metals may be performed as follows:—

From antimony. The mixed sulphides are oxidised with *aqua regia*, as already described, and tartaric acid solution added, followed by excess of ammonium chloride and ammonia. The latter should produce no opalescence. If a precipitate is produced, a further quantity of tartaric acid or ammonium chloride must be added. The solution is then precipitated by 'magnesia mixture,' and the estimation made as before described.

From tin. A solution of oxalic acid is added to the solution in the proportion of 20 grams of oxalic acid for each gram of tin supposed to be present. The solution should be sufficiently strong for the acid to crystallise out on cooling. The liquid is heated to boiling and sulphuretted hydrogen passed through for 20 minutes, The liquid is allowed to stand for about 30 minutes, and the arsenious sulphide filtered off. It is quite free from tin.

Arsenious chloride in small quantities may be separated from other metals by distillation of the hydrochloric solution (Thorpe, Chem. Soc. Trans. 83, 971); in certain metals and alloys by distillation of the finely divided material with a suitable solution of ferric and calcium chlorides, acidified with hydrochloric acid (the materials used should be tested for arsenic). With a solution of zinc and cupric chlorides in hydrochloric acid boiling at 108° both arsenic and antimony may be separated from other metals; the arsenic is in the distillate from 108° to 115°, the antimony in the distillate from 115° to 160° (Gibb, J. Soc. Chem. Ind. xx. 3).

For the estimation of arsenic in ores, Parnell recommends the following method:—A weighed quantity of the *finely powdered* ore is heated to about 200° in a slow current of chlorine gas, the volatilised arsenious chloride being absorbed in a solution of chlorine water. After evaporation of the excess of chlorine, the arsenic may be estimated by any ordinary method. Antimony, if present in the ore, would also volatilise with the arsenic.

For technical purposes the following methods are largely used:—

A weighed portion is partially decomposed with a minimum quantity of strong nitric acid, dried and fused with sodium peroxide or a mixture of sodium carbonate and nitre. The fused mass is extracted with water and filtered. The solution of alkaline arsenate is acidified with nitric acid and boiled to effect decomposition of either peroxide or nitrite; it is next carefully neutralised and then acidified with acetic acid, and the arsenic determined by titration with a standard solution of uranium acetate. Pearce recommends separation as silver arsenate from the aqueous extract after fusion; the silver salt is dissolved in dilute nitric acid and estimated by Volhard's method. With very poor ores to the solution in nitric acid a sufficient quantity of tartaric acid is added, and the arsenic separated as magnesium ammonium arsenate. For the estimation of arsenic in organic salts ignite with sodium peroxide, reduce with hydriodic acid and titrate with iodine and starch in presence of disodium hydrogen phosphate (Morgan, Chem. Soc. Trans. 1909, 95, 1477).

Alloys of arsenic.

Arsenic combines with most metals, in many cases in atomic proportions, the alloys being then known as arsenides. Many natural arsenides occur as minerals.

The alloys may be prepared (1) by fusing the metals under a layer of borax, or in an

atmosphere of some inert gas; (2) by reducing the arsenite or arsenate of the metal with potassium cyanide; and (3) in some cases—as with gold, silver, and copper—by placing arsenic in a solution of a metallic salt. W. Spring (Ber. 16, 324) has obtained crystalline alloys of arsenic with other metals by repeatedly compressing a mixture of the constituents at 6500 atmospheres.

When heated out of contact with air, arsenical alloys usually lose a portion of their arsenic; heated in air the arsenic is oxidised, a portion volatilising, and the remainder forming an arsenite or arsenate of the metal. When heated with nitre, arsenates are produced. (For a list of alloys of arsenic in atomic proportions, probably existing as arsenides, *v.* A. Descamps, Compt. rend. 686, 1022 and 1065.) Some ancient copper spear-heads from Cyprus contained 1·348 p.c. arsenic, and a bronze figure of the Ptolemaic period from Egypt contained 1·479 p.c.

The presence of arsenic generally renders an alloy more brittle, more fusible, and brighter. In Pattinson's process it tends to render the crystals smaller, and thus lengthens the time required for draining. Its alloys with iron, zinc, and tin are brittle; with gold and silver, brittle, and grey; and with lead and antimony, hard, brittle, and fusible. The addition of from 3 to 6 parts arsenic to 1000 lead (with occasionally a little copper) causes the small shot in falling down the tower to form spheres, instead of elongating, as they have otherwise a tendency to do. The arsenic is frequently added in the proper proportions in the form of an alloy of lead and arsenic known as 'temper'; this is prepared by fusing together arsenious oxide and lead. By heating a mixture of lead and arsenic to whiteness, Berthier obtained an alloy of the formula Pb_4As, any excess of arsenic beyond that corresponding to this formula being volatilised at that temperature. With copper it forms white, malleable, dense, and fusible alloys. White copper contains about 10 p.c. arsenic. Arsenic is also used in speculum metal, and

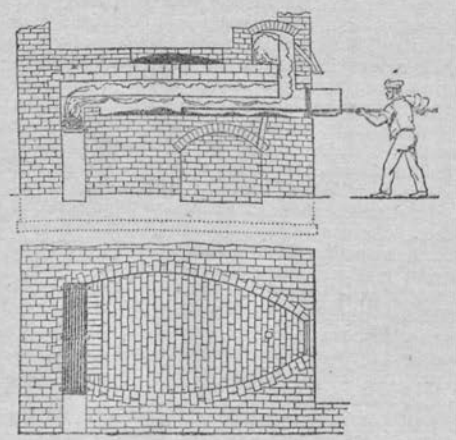


Fig. 1.

is frequently present in common Britannia metal.

With potassium and sodium arsenic forms alloys which evolve arseniuretted hydrogen when placed in water. With platinum it forms a fusible alloy, and was formerly used to facilitate the working of that metal.

Arsenic trihydride. *Arsenetted or arseniuretted hydrogen. Arsine.* AsH_3. This gas is formed whenever hydrogen is liberated in a solution containing arsenious acid or an arsenite, as when zinc is introduced into an acid solution of the substance. It is a colourless, neutral, disagreeably smelling gas, slightly soluble in water, and highly poisonous, even when much diluted. At a red heat it decomposes into arsenic and hydrogen.

It is evolved in the bronzing of brass with arsenic, in tinning sheet iron and frequently in the desilverisation of lead with zinc and subsequent heating of the argentiferous zinc with acid. It is also occasionally present in the air of rooms of which the wall-paper is coloured with arsenical pigments (*v. Schweinfurth green*). It is a very powerful reducing agent, precipitating silver, gold, and other metals from their solutions. Methods for the quantitative estimation of arsenic are based on this property.

A solid hydride of arsenic appears to exist.

Arsenious oxide. *Arsenious acid. White arsenic. Flowers of arsenic; commonly known as 'arsenic.'* As_4O_6.

Preparation.—In Cornwall, Devon, and at Swansea, arsenious oxide is principally prepared by roasting mispickel, which occurs mixed with iron and copper pyrites, tin ore, wolfram, blende, galena, &c. These ores, if present in sufficient quantity, are separated as far as possible before roasting; tinstone by washing the finely powdered ore, and the other minerals by hand. Arsenious oxide is also largely prepared by roasting arsenical silver at Andreasberg, and from arsenical ores of nickel and cobalt.

In ores from which arsenic is produced as a principal product, the arsenical pyrites generally occur to the amount of about 12 p.c.

The ores are usually roasted in a reverberatory furnace. In a common form, the furnace bed is flat, 12–15 feet long and 7–9 feet wide in the middle; the arch is about 2 feet above the bed, and sinks gradually towards the flue, at which end there is an iron door, through which the ore is raked (Fig. 1).

From 8–15 cwt. of the stamped dried ore is introduced through a hopper over the centre of the fire-bridge and spread over the furnace bed. The heat is raised to dull redness and the ore is frequently stirred to ensure thorough oxidation of the arsenic and sulphur. In about 10 hours these have been expelled as oxides, and the arsenious oxide together with some of the sulphur collects in the flues. The spent ore is removed through an aperture in the bed, which is closed with an iron door during calcination.

Two such furnaces are sometimes built side by side, separated by a wall, and with their flues uniting. The furnace beds slope gently towards a narrow fireplace. In the first instance the ore is introduced through a number of doors on each side of the furnace. As the ore is worked downwards its place is constantly supplied by fresh ore through an opening in the roof.

Brunton's Calciner is much used in Cornwall.

It is practically a reverberatory furnace with a revolving bed. The bed is of firebrick resting on a cast-iron table, and is higher at the centre than at the periphery. It is usually 8 or 10 feet in diameter; it revolves three or four times in an hour by steam or water power, about half-horse power being required. There are two furnaces on opposite sides of the bed.

The dried and finely stamped ore is introduced through a hopper over the centre of the bed. Above the bed are fixed radially three cast-iron frames in which are fastened a number of equidistant iron scrapers shaped like the coulter of a plough and placed obliquely, so that, as the bed revolves, they turn the ore over and outwards towards the periphery of the bed. It is thus thoroughly roasted, and, on reaching the edge, falls into the chamber beneath.

Oxland and Hocking's Patent Calciner (English Pat. 1868, 2950) is largely used, especially for 'rank' ores (Figs. 2 and 3). It consists of a wrought-iron cylinder, which, if 32 feet in length, is lined with sufficient firebrick to leave 4 feet clear internal diameter. Four longitudinal ribs of firebrick occur within the furnace, leaving sufficient space at the upper end for the continuous supply of the ore. The cylinder is generally mounted in an inclined position, the slope being usually $\frac{1}{2}$ to 1 inch per foot, and is turned by means of a turbine or water-wheel once in 8 or 10 minutes upon friction-wheels.

The dried, finely powdered ore is introduced through an archimedean screw, or from a hopper at the upper end, and in the revolution of the tube becomes lifted to a certain height by the ribs of firebrick, and falls in a fine stream through the hot blast. In a few revolutions the ore is completely oxidised, the arsenic burning off first, and finally reaches the lower end of the tube, where it falls through a chamber beneath. A calciner of the above size will roast 6 to 7 tons of ore in 24 hours. In this furnace the amount of air required is minimised, thus rendering the condensation less difficult. The amount of fuel used is also small (*v.* further, Henderson, Proc. Roy. Inst. Mech. Engineers, 1873).

A modification of this furnace was patented by R. & C. Oxland (Eng. Pat. 7285, 1885). It is so arranged that the products pass into the condensing chambers unmixed with other gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a grate and a system of flues surrounding it. At the end of the prolongation is a door for removing the calcined products and a regulator for admitting the required amount of air.

Roasting in muffle furnaces.—This process is used at Altenberg (Figs. 4, 5, and 6) and at Reichenstein in Silesia (Figs. 7 and 8), where wood is cheap.

The ore, reduced to a moderate size and known as *schleich*, is introduced through an opening in the top in charges of about 10 cwt. and spread 2 or 3 inches thick on the floor of the muffle. It is first heated to redness, and then more gently, with the muffle door open, to oxidise the mass thoroughly before sublimation. The operation is completed in 11 or 12 hours.

Condensation of the oxide.—The vapours passing off in the roasting are carried through chambers so arranged that the gases come in contact with a very large condensing surface passing through a series of chambers before escaping into the air. At the Devon Great

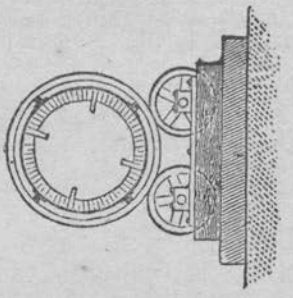


Fig. 3.

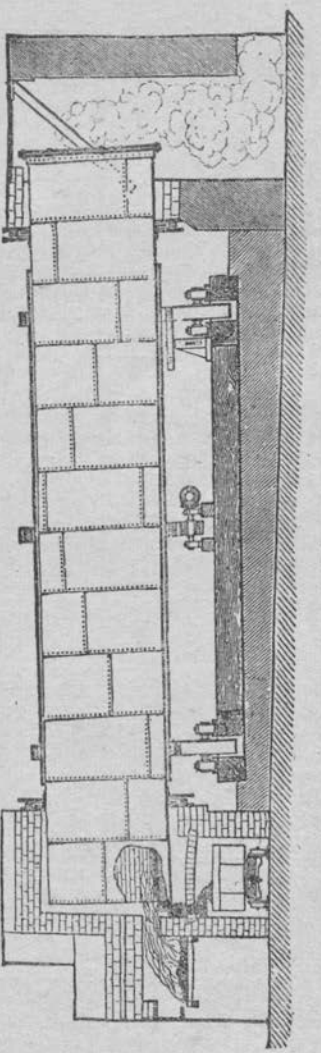


Fig. 2.

Consols and other large works, the chambers are made of thin brickwork covered with iron plates to assist the cooling of the gaseous oxide.

The ores, before calcination, are dried over iron plates on the condensers.

These chambers are cleared at intervals,

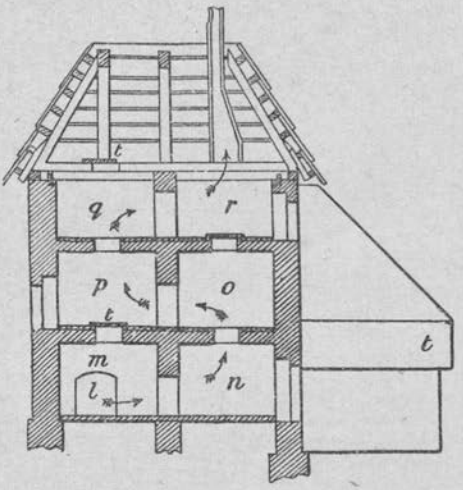


FIG. 4.—VERTICAL SECTION OF 'POISON TOWER.'

some every fortnight, those at Silesia once in two months. Two sets of chambers are frequently used, so that one set may be working while the other is being cleared.

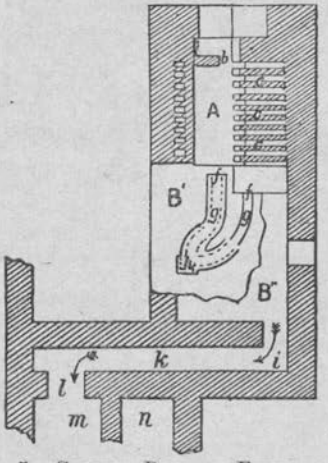


FIG. 5.—GROUND PLAN OF FURNACE.

The oxide produced by all processes except that of the muffle is known as 'arsenical soot,' and is impure, containing carbon and sulphur compounds; when so mixed it is of a dark-grey colour and requires to be resublimed.

The condensing chambers connected with the muffles in Silesia are in a lofty building called the 'poison tower' (*Giftthürme*). The gases traverse, by a sinuous course, a series of chambers, depositing the finest product in the lower ones, that in the upper chambers containing sulphur. The chambers are cleared about every 2 months, and contain about 25 tons of white arsenic ('poison flour,' or *Giftmehl*). Being comparatively pure, it does not usually require refining, but may be at once converted into arsenical glass. The workmen engaged in clearing the chambers are clothed in leathern garments with glazed apertures for the eyes, and wear wet cloths over their mouths and noses to absorb the irritating fumes. It is stated at Salzburg that only 'arsenic-eaters' can perform this work continuously.

Refining or resublimation.—For this purpose a reverberatory furnace is used, which is usually much shorter than that in which the calcination is performed. The arsenical soot is charged from the top and paddled down through doors at the side, more being added as it sublimes. The fuel used is smokeless, usually a mixture of anthracite and coke.

The sublimate is collected in chambers similar to those already described. It is white, glistening, and minutely crystalline. It is ground between millstones, and is thence fed into kegs from a hopper through a leathern hose which fastens to the top of the cask and prevents any escape of the powder.

Arsenic glass, or vitreous white arsenic, is prepared by volatilisation of the powder under slight pressure. For this purpose, at Swansea, a cast-iron pan is used 2 feet in diameter and surmounted by a bell 2 feet 6 inches high. The pan is heated to a cherry red, and about ¼ cwt. of refined white arsenic introduced through an opening in the top of the bell, which is then closed with a plug. In about 2 hours the whole has evaporated and condensed on the bell as a transparent glass; more white arsenic is then introduced and condensed, until after 24 hours the glass has reached a thickness of about 1 inch. The later charges, owing to the condensing surface being hotter, require about twice as long to condense as the first.

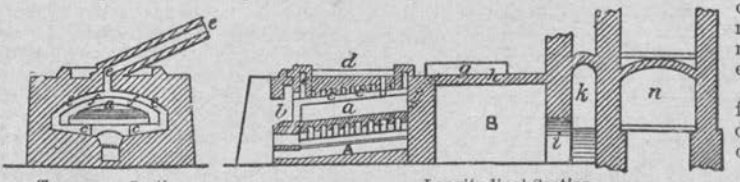
At Silesia the subliming pots are deeper and of greater capacity; they are surmounted by iron drums and conical caps, which condense the 'glass' and open into condensing chambers. The temperature is carefully regulated. The arsenic glass produced amounts to about 92 p.c. of the 'flowers' used.

Analyses of Arsenic Powder and Arsenic Glass.

(1) Powder from Altenberg, from the condenser of a tin roasting furnace, near the furnace end (Lampadius).

(2) Do. from further end of condenser (Lampadius).

(3) Do. from Oberschlema (Lampadius).



Transverse Section. Longitudinal Section.

FIG. 6.—SUBLIMING FURNACE.

(4) Arsenic glass from Andreasberg (Streng).

	(1)	(2)	(3)	(4)
Arsenious oxide .	90·1	95·85	94·31	98·2
Arsenious sulphide .	2·05	0·32	1·03	—
Bismuth. . .	—	—	0·25	—
Sulphur . . .	0·73	0·71	0·50	—
Ore-dust . .	5·51	2·05	3·05	—
Antimonious oxide .	—	—	—	1·68

Properties and uses of arsenious oxide.—White arsenic occurs in the amorphous or glassy

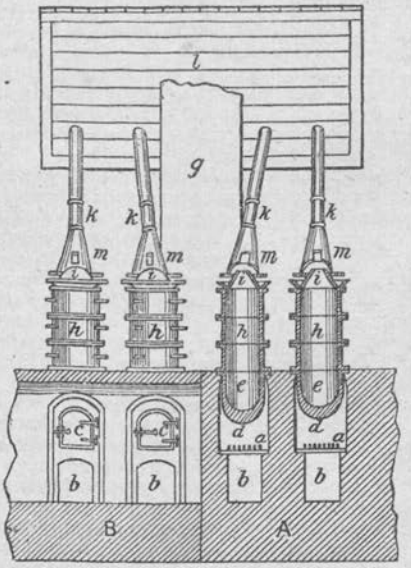


FIG. 7.

form, and in two crystalline modifications: (1) the octahedral or common form, and (2) in trimetric prisms, occasionally found in sublimates; this form is converted into the octahedral variety when heated or boiled in water.

The amorphous form is transparent when first prepared, but becomes opaque when exposed to the air, especially when damp, diminishing

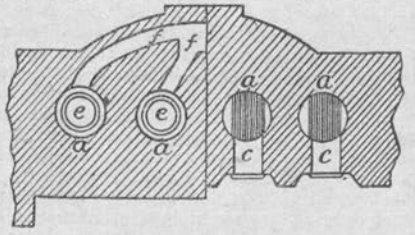


FIG. 8.—REICHENSTEIN FURNACES.

slightly in specific gravity and forming the crystalline oxide. The action commences at the outside, so that even after a considerable time a piece is frequently found with a transparent nucleus. The vitreous form may be kept in a sealed glass tube unchanged for years.

The vitreous form, according to Buchner, is soluble in 108 parts of cold water, whilst the opaque form requires 355 parts; the solubility of an ordinary piece is therefore doubtful, depending on the amount of change it has undergone. It is very soluble in glycerol, and is stated by Jackson to form *glyceryl arsenite* (Chem. News, 49, 258).

On making a strong solution of the *vitreous* form in dilute hydrochloric acid by dissolving 3 parts in a mixture of 12 hydrochloric acid and 4 water, and slowly cooling, it is deposited in the octahedral form, each crystal as it falls producing a flash of light (H. Rose). If these crystals be redissolved or if the opaque form be used, no light is produced on crystallising, that phenomenon appearing to depend on the change of the amorphous into the crystalline form at the moment of crystallisation.

At about 193° arsenious oxide softens and sublimes without fusion; it fuses under pressure; its vapour is colourless and odourless. It is acid to test papers, but does not appear to form true arsenious acid on solution in water.

Arsenious oxide is a powerful febrifuge, being sometimes efficacious when quinine has failed. It is highly poisonous, 2 or 3 grains being a very dangerous dose. When used habitually, however, comparatively large quantities may be taken with impunity. The inhabitants of Styria eat it under the name of 'hydrach,' to increase their endurance. Many authentic cases are recorded of 6 grains and upwards being taken without ill effect. Arsenic-eaters are stated to be fresh complexioned, with a tendency to stoutness, to be long-lived, but to die suddenly. The workmen engaged in the manufacture of dyes where arsenic acid is used have been observed to have this tendency to stoutness (*v.* Roscoe, Mem. of Lit. Phil. Soc. Manchester, 1860). In cases of death from poisoning, the greater part of the arsenic appears to be contained in the liver and intestines; of the bones, those of the pelvis and neighbourhood vertebræ appear to contain most.

In manufactures, arsenious oxide is used: in glass-making, to remove the colour produced by the lower oxides of iron; in enamelling; in calico-printing; as a constituent of white fire in pyrotechny; for the prevention of boiler incrustations (40 parts white arsenic to 9 sodium carbonate); in the manufacture of arsenic acid; and of fly and rat poisons; and in the manufacture of a large number of pigments, arsenic being found in green, blue, pink, white, brown, and other colours. As a preservative it is thrown into the holds of ships, to prevent vegetable decomposition; as a wash for walls in India, to prevent insect ravages; to prevent smut in wheat; and with sodium carbonate as a wash for sheep; and in arsenical soap, for preserving skins.

Arsenious oxide is employed in the fixation of aniline colours, especially of aniline blue. It is used principally for preparing steam colours, either as a solution in glycerol containing 4 lbs. of the oxide to 1 gallon of glycerol, under the name 'arsenic and glycerine standard'; or as sodium arsenite, dissolved in sodium carbonate or borate.

In medicine it is used as Fowler's solution, which contains 4 grains of the oxide (in the form of sodium arsenite) in each ounce of fluid. In India it has been used as a cure for hydrophobia and serpent poisoning. In veterinary

surgery it is largely used as a tonic, to eradicate worms, and for improving the coats of horses.

It occurs, either as an impurity or as an adulterant, in a large number of commercial products. Besides the ordinary commercial compounds in which arsenic is expected to be present, it has been found in caustic soda, potassium chlorate, commercial glucose (Clouët and Ritter), and in wine free from artificial colouring matter (traced to sulphuric acid used in purifying the casks). Dr. Tidy found about 38 p.c. of arsenious oxide in some 'violet powder' which had caused the death of at least two children (Lancet, Aug. 21, 1878).

In the year 1900 occurred a serious epidemic of arsenic-poisoning due to contamination of beer through the use of brewing sugars, glucose, or 'invert' sugar containing arsenic. The arsenic was introduced by the use of highly arsenical sulphuric acid in the production of the sugars. The total number of persons who suffered in consequence of the epidemic was certainly 6000, and probably considerably greater. At least 70 deaths were attributed to the epidemic.

Coal or coke used for malt drying always contains arsenic; with an ordinary malt kiln part of the arsenic volatilises and may deposit on the malt. Various methods have been tried and adopted in which it has been found that access of arsenic to malt may be obviated or diminished (Royal Commission: Arsenical Poisoning, 1903).

(For a statement of the amount of arsenic in the varieties of pyrites, and of its distribution in the preparation of sulphuric acid and alkali, *v.* H. Smith, Phil. Mag. [4] 44, 370; Chem. News, 26, 176; and C. Hjelt, Dingl. poly. J. 226, 174–181.)

Fresenius finds that the arsenic in many chemical glasses is removed by alkaline, but not by acid liquids; the bearing of this on judicial investigations is important.

The commercial article is frequently adulterated with gypsum, chalk, &c., these may easily be detected by heating a little on a knife, when they will remain after the oxide has volatilised.

Sodium arsenite. *Acid sodium arsenite*

$$Na_2O{\cdot}2As_2O_3{\cdot}2H_2O$$

is prepared by dissolving arsenious oxide in a solution of caustic soda or sodium carbonate, and evaporating the solution. The neutral salt, $Na_2O{\cdot}As_2O_3$, is formed by boiling this compound for some time with sodium carbonate, and washing the residual salt with alcohol (Pasteur).

Potassium arsenite is prepared in a similar manner.

Sodium arsenite is used as a substitute for dung in dyeing, but is not so reliable as the arsenate. It enters anto the composition of all preparations in which arsenious oxide is dissolved with sodium carbonate.

An arsenite of chromium and iron is used as a green pigment in wall-papers.

Scheele's green. *Arsenite of copper. Hydrocupric arsenite.* $CuHAsO_3$.

According to Scheele's method, 11 oz. arsenious oxide are gradually added to a solution of 2 lbs. potassium carbonate in 10 lbs. boiling water; this is filtered and poured into a solution of 2 lbs. copper sulphate in 30 lbs. water, so long as a grass-green precipitate falls. The precipitate is thrown upon a filter cloth, washed with warm water, and dried gently with the production of about 1½ lbs. of the pigment.

Scheele's green is a pulverulent, fine light-green colour, formerly largely used in calico-printing and for wall-papers. It is, however, much less used at the present time. It dissolves entirely in excess of alkali or in acids.

Schweinfurth green. *Imperial green. Emerald green. Mitis green. Aceto-arsenite of copper* (when mixed with gypsum or heavy spar, known also as *Mountain* or *Neuwieder green*).

$$3CuOAs_2O_3{\cdot}Cu{\cdot}(C_2H_3O_2)_2.$$

Five parts of verdigris (basic copper acetate) are made into a thin paste with water and added to a boiling solution of rather more than 4 parts arsenious oxide in 50 parts water; the solution is kept boiling during the mixture. If a yellow-green precipitate falls, a little acetic acid is added, and the solution boiled a few minutes longer; the precipitate becomes crystalline and soon acquires the characteristic green colour.

A very fine product is prepared by the following method:—Boiling, concentrated solutions of arsenious oxide and copper acetate are mixed in such proportions that equal weights of the two substances are present when a bulky olive-green precipitate falls; an equal bulk of cold water is then added and the mixture placed in a flask which it fills to the neck, thus preventing any pellicle which may form on the surface from falling through the liquid and causing a premature crystallisation. The colour under these circumstances takes two or three days to perfect, the beauty of the product being much increased by slow formation. The workmen engaged in the preparation of this pigment do not appear to be injured by it. In contact with organic matter it is, however, liable to change. Bischoff (Zeitsch. anal. Chem. 23, 117) states that micro-organisms and fungi act on compounds of arsenic, producing arseniuretted hydrogen; and Fleck, Sonnenschein, and others have conclusively shown that this gas is frequently present in the air of rooms with arsenical wall-paper. By the action of damp and mould on paper coloured with this pigment a peculiar odour is frequently produced, which appears to be due to the formation of diethylarsine (*v.* ARSENIC MOULD).

Arsenic oxide. *Arsenic acid, Arsenic pentoxide, Acide arsénique, Arsensäure, Acidum arsenicum.* As_2O_5.

Produced when arsenious oxide is acted upon by an oxidising agent.

On the large scale 4 parts white arsenic are gradually added to 3 parts nitric acid of not less than 1·35 sp.gr. in a vat capable of holding from 65 to 70 kilos. of white arsenic. Great heat is produced and the evolved fumes are passed over coke moistened with water, whereby about two-thirds of the nitric acid is recovered. In 24 hours a syrupy liquid is formed, containing a small quantity of arsenious oxide, which may be oxidised with a little more nitric acid.

Kestner performs the oxidation in large glass flasks, the nitrous fumes being passed through lead pipes and condensed in leaden chambers.

Arsenic oxide has also been prepared by suspending arsenious oxide in water, passing a current of chlorine through the liquid, and evaporating the solution thus produced.

It is a deliquescent solid fusing at a dull-red

heat, of acid metallic taste and acid reaction. It dissolves in 6 parts cold and in 2 parts hot water. A cold, strong solution blisters the skin. Arsenic oxide and its salts are less poisonous than the corresponding arsenious compounds.

Sodium arsenate. *Hydric disodic arsenate*; *Dung salt.*' Na_2HAsO_4.

It is prepared by saturating arsenious oxide with crude soda ash, drying, and deflagrating with sodium nitrate in a reverberatory furnace.

Arsenate of soda is largely used in calico-printing as a substitute for dung, its feebly alkaline properties rendering it useful for that purpose.

Arsenate of iron is an amorphous green powder containing 33·6 p.c. arsenic.

Arsenic sulphides. Arsenic forms three well-defined sulphides, As_2S_2, As_2S_3, and As_2S_5, the two former occurring naturally. A large number of other sulphides of indefinite composition also exist.

Realgar. *Disulphide of arsenic. Ruby sulphur. Rothes rauschgelb. Rothes Schwefel. Sulphuré rouge. Orpin rouge. Risigallo. Sandaraca.* As_2S_2.

Prepared by fusing together arsenic and sulphur or orpiment in the proper proportions. On the large scale it is obtained by distilling a mixture of arsenical ores, such as arsenical and iron pyrites, with sulphur or with the sulphide of arsenic precipitated in the purification of sulphuric acid.

The mixture should contain about 15 p.c. arsenic and 26–28 p.c. sulphur; it is placed in flask-shaped earthenware retorts, holding about 60 lbs. when two-thirds full, which are connected with similar receivers. The retorts are gradually heated to redness and kept so for 8–12 hours. The crude realgar should be compact, dark, and rich in arsenic; if sulphur be in excess it is friable and light red. It is re-melted rapidly in cast-iron pans with the requisite amount of sulphur or arsenic, or with realgar of poorer quality. The mass is cleared of slag and heated until quite fluid, and until a small quantity shows the proper appearance on cooling. It is then poured into conical sheet-iron moulds.

Greater care is necessary in the preparation of realgar than of orpiment, and an assay is frequently made to ascertain the exact proportions required before the final melting.

It is hard and brittle, generally opaque, with vitreous conchoidal fracture, orange or hyacinth red in mass and orange-red in powder. Its sp.gr. is 3·4–3·6, and its usual composition is arsenic 75, sulphur 25. It volatilises easily before the blowpipe with a smell of garlic and burning sulphur, is insoluble in water or hydrochloric acid, but soluble in alkaline sulphides.

Realgar is a constituent of blue fire and of 'white Bengal fire,' which is used as a signal light, and consists of realgar 2, sulphur 7, potassium nitrate 24.

The finest variety, especially that which occurs native, is used as a pigment by artists.

Orpiment. *Operment. Gelbes Rauschgelb. Risigallum. Auripigmentum* (of which its usual name is a corruption). *Yellow Sulphide of Arsenic.* As_2S_3.

This sulphide is formed as a yellow precipitate when sulphuretted hydrogen is passed through a solution of arsenious acid in hydrochloric acid.

Schultze (J. pr. Chem. 25, 431) considers that another form of the trisulphide exists which is soluble in water (*v.* COLLOIDS).

On the large scale it is prepared by subliming sulphur with arsenious oxide, 2 parts of arsenious oxide and 1 part sulphur being a common proportion; the colour of the product is lighter when less sulphur is used.

According to R. Wagner, a very fine colour may be produced as follows:—2 parts finely ground barium sulphate are calcined with 1 part powdered charcoal or other carbonaceous matter, and the product is pulverised, mixed with 1 part ground orpiment, boiled in water and filtered. The solution, containing a sulpharsenite of barium, is precipitated by the addition of sulphuric acid. By the addition of a suitable amount of barium chloride before precipitation, the pigment may be correspondingly lightened in colour.

Orpiment is insoluble in water but very soluble in alkaline sulphides. It was formerly much used as a pigment under the name of King's Yellow, but now is largely replaced by chrome yellow. The lighter varieties contain as much as 80 to 90 p.c. of arsenious oxide, and are consequently very poisonous. The darker varieties contain from 1 p.c. to 15 p.c. of the oxide and from 0·2 to 3 p.c. non-volatile matter. It is used in pyrotechny, and the finer kind, especially the mineral, is made into pigment for artists.

It was formerly used as a deoxidising agent in the reduction of indigo blue, and in ammoniacal solution in silk-dyeing. A mixture of 9 orpiment and 1 quicklime made into a paste with water is used under the name of 'Rusma' for removing hair from skins, but is now generally replaced by the solution of sulphide of lime prepared from the spent lime of gasworks.

Arsenic pentasulphide As_2S_5. Berzelius in 1826 stated that this compound was formed when sulphuretted hydrogen is passed through a moderately concentrated solution of arsenic acid, but the precipitate was generally considered to be a mixture of the trisulphide and sulphur. Bunsen in 1878 showed that it was produced on passing a rapid current of sulphuretted hydrogen through a hot hydrochloric acid solution of an alkaline arsenate, and his results were confirmed by McCay in 1887 (*cf.* Brauner and Tomiček, Chem. Soc. Trans. 1888, 147).

Arsenic pentasulphide is totally insoluble in water, alcohol, or disulphide of carbon. The dry substance, on rubbing in a mortar, becomes strongly electrical.

Arsenic chloride. *Butter of arsenic. Caustic oil of arsenic* $AsCl_3$ is produced by the action of chlorine on arsenic; by distilling arsenic with mercuric chloride; and by distilling arsenious oxide with strong hydrochloric acid. It is a colourless, oily liquid, of sp.gr. 2·205 0°/4° boiling at 130·2° (Thorpe).

The chloride and iodide are used to a slight extent in medicine. H. W. H.

ORGANIC COMPOUNDS OF ARSENIC.

Cacodyl oxide (*Dimethyl arsine oxide*) $[As(CH_3)_2]_2O$ is formed by the dry distillation of a mixture of equal parts of potassium acetate

and arsenic trioxide. As thus obtained, it is spontaneously inflammable owing to the presence of free cacodyl. When pure, it is an oily liquid, b.p. 150°, insoluble in water, and of a powerful and nauseous odour. It is extremely poisonous. With acids it forms salts, such as *cacodyl chloride* $As(CH_3)_2 \cdot Cl$; this, on heating with metallic zinc, in absence of air, yields *cacodyl* $As_2(CH_3)_4$, as a colourless, liquid, which takes fire on exposure to air. This compound also has an intensely disagreeable smell, and is very poisonous.

Cacodylic acid $(CH_3)_2 \cdot AsO \cdot OH$ is obtained by the oxidation of cacodyl oxide by means of mercuric oxide. It is a crystalline, odourless substance, and is not poisonous (Bunsen; Marshall and Greene, Amer. Chem. J. 8, 128). The salts of cacodylic acid, especially the sodium, magnesium, and strychnine salts, have been used in medicine, but have fallen into disfavour on account of their lack of arsenical effect, and of certain unpleasant effects attendant upon their use.

Disodium methylarsenate, 'arrhenal' (*'New cacodyl'*) $CH_3 \cdot AsO(ONa)_2$ is prepared by the interaction of methyl iodide and sodium arsenate in the presence of excess of alkali. It is a white crystalline compound, easily soluble in water, but only slightly soluble in alcohol. It may be distinguished from sodium cacodylate by means of mercuric chloride, which gives a reddish-yellow precipitate with arrhenal, but a white precipitate with the cacodylate (Martindale, J. Chem. Soc. Ind. 1907, 907).

The compounds of arsenic with aromatic radicles, especially *atoxyl* and its congeners, have attained importance in the treatment of 'sleeping sickness,' Gambia fever, &c., which are due to the presence of specific trypanosomata in the blood (*v.* Plimmer and Thomson, Proc. Roy. Soc. B. 1907, 505).

Diphenylarsinic acid (*Phenyl cacodylic acid*) $(C_6H_5)_2 : AsO \cdot OH$ is prepared as follows: Diphenyl-arsenious chloride, one of the products of the interaction of mercury diphenyl and arsenious chloride (Michaelis, Ber. 8, 1316; 9 1566), is mixed with water and treated with a rapid stream of chlorine at a temperature of 60°–70°.

Diphenylarsinic chloride $(C_6H_5)_2AsCl_2$ is thus formed: the solution is evaporated to dryness on the water-bath, and the residue taken up with water, from which the acid can be crystallised in long needles; m.p. 174° (Michaelis, Annalen, 201, 231; 321, 151). Martindale recommends the use of ether as a solvent. (For an alternative method of preparation, *see* Sachs and Kantorowiez, Ber. 41, 2767.)

***p*-Tolylarsinic acid** $CH_3 \cdot C_6H_4 \cdot AsO(OH)_2$ is prepared by passing chlorine into a mixture of 1 part *p*-tolyl-arsenious chloride and 5 parts water at 60°–70°. The solution is evaporated to dryness and the residue boiled with water, from which the acid crystallises (Martindale). The acid has been found efficacious in destroying trypanosomes (Plimmer and Thomson, *ibid.*).

***p*-Aminophenylarsinic acid** (*Arsanilic acid*) was first prepared by Béchamp in 1863 (Compt. rend. 56, 1172), by heating aniline arsenate at 190°–200°. He supposed it to be an anilide of arsenic acid. Ehrlich and Bertheim have shown (Ber. 40, 3292) that the acid has the composition expressed by the formula $NH_2 \cdot C_6H_4 \cdot AsO(OH)_2$. It is weakly basic, and forms salts with acids which are at once hydrolysed by water.

Sodium *p*-aminophenylarsinate, known as *'atoxyl'* (*arsamin, soamin*) $NH_2 \cdot C_6H_4 \cdot AsO(OH)ONa$, is obtained by neutralising the above acid with soda. It is a white salt, crystallising with an amount of water variously stated to be between 2 and 6 molecules, and effloresces on exposure to air (Moore, Nierenstein and Todd, Biochem. Jour. 1907, 300; *v.* also Ehrlich and Bertheim). The anhydrous salt is soluble in methyl alcohol, but almost insoluble in ether, acetone, benzol, or chloroform. (For its therapeutic action, *see* Pharm. Chem. Jour. 1907, 528.) It is at present the compound of arsenic most largely used in combating trypanosomes.

Atoxyl solutions should be made with cold, boiled water and kept in the dark. They must not be allowed to become alkaline, and should be boiled for two minutes (not more) before use.

(For a method of estimating either arrhenal or atoxyl, *v.* Bougault, J. Pharm. Chim. 1907, 13.)

Mercury *p*-aminophenylarsinate (*Asyphil*) has been suggested as a substitute for atoxyl. It may, in common with many other insoluble organic compounds of arsenic, be dissolved in glycerol, and this solution, strong or diluted, used for injection. It is said that such a solution has a stronger action on trypanosomes than has atoxyl (P. Wolff, Ger. Pat. 213394, 1908).

Acetyl-*p*-aminophenylarsinic acid (*Acetyl-arsanilic acid*) $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot As(OH)_2$ is prepared by acetylating 31 parts of atoxyl with 55 parts of acetic anhydride, and then adding 300 parts of water and 52 parts hydrochloric acid (Ber. 40, 3292). By neutralising the acid with soda,

Sodium acetyl-*p*-aminophenylarsinate (*'Arsacetin,' acetyl-atoxyl*) $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot AsO(OH) \cdot ONa$ is obtained as a white crystalline powder, soluble in water (1 : 10). This compound is stated to be less toxic than atoxyl (*v.* Extra Pharmacopœia, xiii. 168), and its solutions can be sterilised by heat and stored without alteration. It has been successfully exhibited in cases of syphilis, and is very active in combating trypanosomes.

Phenylglycine-*p*-arsinic acid

$$CO_2H \cdot CH_2 \cdot NH \cdot C_6H_4AsO(OH)_2$$

is prepared either by mixing sodium *p*-aminoarsinate ('atoxyl') and chloroacetic acid in hot water, or by hydrolysing with alkalis the nitrile $CN \cdot CH_2 \cdot NH \cdot C_6H_4AsO(OH)_2$ produced by warming together in aqueous solution, *p*-aminophenylarsinic acid, potassium cyanide and 40 p.c. formaldehyde (D. R. P. 204664).

Arsenophenylglycine ('418')

$$As_2(C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H)_2,$$

a reddish-brown powder, soluble in aqueous sodium carbonate, but insoluble in dilute mineral acids, and the ordinary organic media, is prepared by reducing the preceding compound with alkaline sodium hyposulphite (D. R. P. 206057; U.S. Pat. 888321). This substance has given promising results in sleeping sickness. Ehrlich supposes that it acts on that part of the trypanosome concerned with multiplication. The sodium salt is a readily soluble yellow powder, which, however, can be preserved only in sealed

tubes; it has found employment in a 5 p.c. ointment in eye affections and eczema.

***p*-Hydroxyphenylarsinic acid**

$HO{\cdot}C_6H_4{\cdot}AsO(OH)_2$,

yellow prisms; m.p. 173°–174°, is obtainable either directly by heating phenol and crystallised arsenic acid at 150° for 4 hours, or by decomposing with hot water the diazonium derivative of *p*-aminophenylarsinic acid.

2-Nitrophenol-*p*-arsinic acid

$HO{\cdot}C_6H_3(NO_2){\cdot}AsO(OH)_2$,

is prepared by dissolving the sodium salt of the preceding acid in cold concentrated sulphuric acid and adding to the solution at 0° the calculated amount of nitric acid (sp.gr. 1·4) mixed with an equal volume of sulphuric acid.

4 : 4′-Dihydroxy-3 : 3′-diaminoarsenobenzene hydrochloride $As_2[C_6H_3(OH).NH_2]_2,2HCl$ (*Salvarsan*, '606') is produced by reducing the preceding compound with sodium sulphide, when the free base separates as a yellow crystalline precipitate, soluble in dilute hydrochloric acid or aqueous alkalis, and reprecipitated from the latter by acetic acid. This compound appears to have a specific action on trypanosomes and spirochetes with a minimum evil after-effect on the host of these parasitic organisms. Very remarkable curative results have been obtained in syphilis, relapsing fever, framboesia, and fowl spirillosis. The drug has also been exhibited with some success in malaria and leprosy; it is applied in the form of injections, which may be either subcutaneous, intramuscular, or intravenous.

When a sufficient dose is administered it is frequently found that complete disappearance of the specific organism is effected after a single injection (*v.* Ehrlich and Hata, Die experimentelle Chemotherapie der Spirillosen (Syphilis, Rückfallfieber, Hühner Spirillose, Framboësie); J. Bresler, Die Syphilisbehandlung mit dem Ehrlich-Hata'schen Mittel; Martindale and Westcott, Salvarsan or '606,' 1911). (For organic arsenic compounds containing two or thre aromatic or hydroaromatic groups, *v.* Chem. Soc. Trans. 1908, 93, 1180, 1893, 2144; 1909, 95, 1473; Ber. 1908, 41, 931, 1672; 1910, 43, 924.)

Arsenogene is an indefinite compound of peptonised casein and arsenic, recommended for medicinal use by Salkowski (Apoth. Zeit. 1908, 114).

The preparation of albuminoid compounds of arsenic has been patented by Klopfer (D. R. P. 214717, 1908) and Gnezda (D. R. P. 201370, 1906).

(For the determination of arsenic in organic compounds, *see* Little, Cahen and Morgan, Trans. Chem. Soc. 1909, 1477.)

ARSENICAL PYRITES or ***Arsenical mundic.*** Names commonly used by miners for the mineral *mispickel* (*q.v.*) or *arsenopyrite* (FeAsS), which is the principal ore of arsenic.

ARSENIC MOULD. *Penicillium brevicaule.* This organism, first obtained by Gosio, in presence of an arsenic compound, forms *diethylarsine* $AsH(C_2H_5)_2$, to which the poisonous gas developed by wall-papers containing arsenic is probably due. The formation of diethylarsine by the action of this mould has been used as a test for arsenic by Markmann (Chem. Zentr. 1900, ii. 1187); Galli-Valerio and Strzyzowski (*ibid.* 1901, i. 63).

Penicillium brevicaule also gives garlic or mercaptan-like odours with compounds of selenium and tellurium (Maassen, Chem. Zentr. 1902, i. 1245).

ARSENOGENE. Trade name for an albuminous preparation of arsenic and iron obtained by heating peptonised casein with arsenic acid and ferric ammonium sulphate. Used in medicine (Salkowski, Apoth. Zeit. 1908, 23, 114).

ARSENOPYRITE *v.* MISPICKEL.

ARSINE. *Arsenic trihydride* (*v.* ARSENIC).

ARTEMISIN. An alkaloid isolated by Merck from the mother liquors obtained in the preparation of santonin from the seeds of *Artemisia maritima.* Forms colourless crystals; m.p. 200°; sparingly soluble in water, more soluble in alcohol; $[\alpha]_D$ −84·3°. With hot soda solution gives a carmine red solution, colourless on cooling. Gives an oxime with hydroxylamine, and a hydrazone with phenylhydrazine (Bertolo, Pharm. J. 1902, 489; Freund and Mai, Ber, 1901, 3717; *cf.* Wedekind and Koch, Ber. 1905, 1845).

ARTICHOKE. Three vegetables are known by this name: (1) the Globe artichoke—the flower head of *Cynara scolymus*; (2) the Jerusalem artichoke—the tuber of *Helianthus tuberosus*; (3) the Japanese or Chinese artichoke—called also Chorogi—the tuber of *Stachys tuberifera.*

The following are analyses of the tubers of the two latter:—

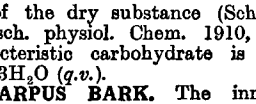
	Water	Protein	Fat	Carbohydrates	Ash
Jerusalem artichoke	79·5	2·6	0·2	16·7	1·0
Stachys tuberifera	78·05	4·32	0·16	14·63	1·21

(Strohmer and Stift, Bied. Zentr. 21, 820.)

The 'protein' of the Jerusalem artichoke includes much material other than true proteid; the carbohydrates consist largely of inulin and levulin.

According to Tanret (Compt. rend. 1893, 117, 50), two other carbohydrates—*helianthenin* m.p. 176°, $12C_6H_{10}O_5+3H_2O$, and *synanthrin*, m.p. 170°, $8C_6H_{10}O_5+H_2O$—are also present, and the levulin or synanthrose described by other observers as occurring in artichokes, is a mixture of saccharose and synanthrin.

The tubers of *Stachys tuberifera* contain many nitrogenous substances of an amide nature—*glutamine, tyrosine, arginine, choline, trigonelline,* and the characteristic body, *stachydrine*



The amount of the last-named is estimated at 0·18 p.c. of the dry substance (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 59). The characteristic carbohydrate is *stachyose* $C_{18}H_{32}O_{16},3H_2O$ (*q.v.*). H. I.

ARTOCARPUS BARK. The inner bark (bast) of the bread-fruit tree [*A. incisa* (Linn.)] is used by the South Sea Islanders for making ropes and clothing. According to Moeller (Dingl. poly. J. 231, 463), this fibre would probably be a very useful one. It can be obtained in large quantities.

ARTOCARPUS INTEGRIFOLIA (Linn. f.). (*Jack Tree*) *v.* JACKWOOD; DYES, NATURAL.

ARUM MACULATUM (Linn.). The common arum, 'wake robin,' or 'lords and ladies,' 'cows and calves,' formerly known as 'abron' janus, 'ramp,' 'starch wort,' contains a starch which was made into a kind of arrowroot in the Isle of Portland, and was the active ingredient of 'Portland powder,' a so-called specific for gout. Occasionally sold in Paris as a cosmetic, under the name of *poudre de Cypre*.

Amorphophallus campanulatus (Blume) is used in India as a vegetable and also in medicine, as are other of the Arums. Many of the Aroideæ act as poisons, their toxic action being due apparently to the irritation induced by the raphides contained in the cells (Pedler and Warden, Jour. Asiatic Soc. of Bengal, 57, 2, 106; Stahl; Pflanzen und Schnecken, Zeitsch. Nat. u. Med. Jena, xxii. N. F. xv. 1888).

ASAFŒTIDA *v.* GUM RESINS.

ASAPROL *v.* ABRASTOL.

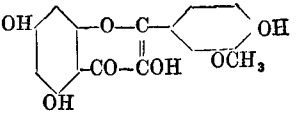
ASARUM CANADENSE (Linn.). A plant indigenous to North America, where it is known by the names of 'Wild Ginger,' or 'Canada Snake-root.' The rhizome yields on distillation an essential oil used in perfumery, containing a phenol $C_9H_{12}O_2$, *d*- and *l*- pinene, *d*-linalool, -borneol, *l*-terpineol, geraniol, eugenol methyl ether, a lactone $C_{14}H_{20}O_2$, a mixture of fatty acids, including palmitic and acetic, and a blue oil of undetermined composition, consisting of oxygenated substances of alcoholic nature (Power and Seed, Chem. Soc. Trans. 1902, 81, 59).

ASBARG. Asbarg consists of the dried flowers and flowering stems of the *Delphinium zalil*, which is found in great quantity in Afghanistan. The dyestuff is collected and taken to Multan and other Punjab towns, from which it is conveyed all over India. It is much used in silk-dyeing for the production of a sulphur-yellow colour known as 'gandkaki,' and, together with *Datisca cannabina*, to obtain a similar shade on alum-mordanted silk; it is also used in calico-printing. The flowers, which are bitter, are likewise employed medicinally as a febrifuge.

The colouring matters of asbarg are present entirely as glucosides, and are best isolated in the crude condition by digesting the boiling aqueous extract with a little sulphuric acid (Perkin and Pilgrim. Chem. Soc. Trans. 1898, 268). A brownish-yellow powder thus separates, which contains three substances: *isorhamnetin*, *quercetin*, and *hæmpferol*.

Isorhamnetin $C_{16}H_{12}O_7$, the sparingly soluble constituent, forms yellow needles resembling rhamnetin in appearance. With lead acetate in alcoholic solution, an orange-red precipitate is formed, whilst ferric chloride gives a greenish-black colouration. Fused with alkali, *phloroglucinol* and *protocatechuic acid* are produced, and when air is aspirated through its alkaline solution, *phloroglucinol* and *vanillic acid* are obtained.

With acetic anhydride *iso*rhamnetin gives a *tetra-acetyl*, derivative $C_{16}H_8O_7(C_2H_3O)_4$, colourless needles, m.p. 195°–196°; and with methyl iodide a *trimethyl ether*, which is identical with *quercetin tetramethyl ether*. As, moreover, by the action of hydriodic acid *iso*rhamnetin yields quercetin, its constitution can only be represented as follows:—



The dyeing properties of *iso*rhamnetin are similar in character to those given by hæmpferol *iso*Rhamnetin is also present in yellow wallflowers (*Cheiranthus cheiri*) (Perkin and Hummel); in red clover flowers, *Trifolium pratense* (Power and Salway, Chem. Soc. Trans. 1910, 97, 245). A description of the more soluble colouring matters quercetin (*quercitron bark*) and hæmpferol (*Delphinium consolida*) are given elsewhere.

In *dyeing properties* asbarg closely resembles quercitron bark, but yields with aluminium mordant, a purer or less orange-yellow. It is, however, a much weaker dyestuff, having but 35 p.c. the dyeing power of quercitron bark. The colouring matter of the flowers, minus the flowering stalks, is present to the extent of 3·47 p.c. A. G. P.

ASBESTOS, from ἄσβεστος, 'unquenched.' Both in ancient and modern times various silicate minerals, closely resembling one another in their finely fibrous texture and flexibility, have been and are still confused under this name. The same is true also of the name 'amianthus' or 'aminatos' (ἀμίαντος, 'undefiled,' because not injured by fire). They are, therefore, collective names of no more definite signification than the adjective 'asbestiform.' Mineralogists are, however, agreed in limiting the name asbestos to the fibrous forms of hornblende, but this limitation is not generally observed. Any ambiguity may be avoided by using the terms amphibole-asbestos (or hornblende-asbestos), serpentine-asbestos, &c., for these asbestiform minerals. The finely fibrous texture is, of course, an accidental character of the mineral species, depending on the enormous elongation in one direction of the individual crystals which form the aggregate. Such a character might, indeed, be assumed by many kinds of minerals; but it is only the following that are of any importance in this connection:—

Tremolite, $CaMg_3(SiO_3)_4$.
Actinolite, $Ca(Mg,Fe)_3(SiO_3)_4$.
Crocidolite, $NaFe'''(SiO_3)_2 \cdot Fe''SiO_3$.
Anthophyllite, $(Mg,Fe)SiO_3$.
Serpentine, $H_4Mg_3Si_2O_9$.
Palygorskite group (pilolite, &c.), $\left\{\begin{matrix} nH_8Mg_2Si_3O_{12} \\ mH_2Al_2Si_4O_{12},5H_2O \end{matrix}\right.$.

The first two of these differ only in the relative proportions of the mutually replaceable magnesium and ferrous iron (and consequently also in their colours, which are white and green respectively), and they are merely varieties of the species amphibole or hornblende. Crocidolite is another species of the amphibole group of minerals, crystallising in the monoclinic system, and also with an angle of 56° between its prismatic cleavages. It is known in the trade as 'blue asbestos,' and it gives the name to the Asbestos Mountains in South Africa, where it is found. Whilst hornblende is more frequently found as stout crystals and compact masses, crocidolite, on the other hand, is as yet known only in the finely fibrous form. Anthophyllite also belongs to the amphibole group, but is orthorhombic in

crystallisation. Some of the asbestos mined in the United States is of this kind. Serpentine occurs in nature as large rock-masses, and the compact rock is frequently traversed by veins of fibrous material of the same composition; the latter is known to mineralogists as *chrysotile*, and in the trade as 'asbestos' or 'Canadian asbestos.' In the minerals of the palygorskite group (A. Fersmann, Bull. Acad. Sci. St. Petersburg, 1908, ii. 255, 637) the fibres rarely show a parallel arrangement, but are more usually matted and interwoven, giving felted masses known as 'mountain-leather,' 'mountain-cork,' and 'mountain-wood.' It is, however, to be remembered that these trivial names may also be applied to similar aggregates of fibrous amphibole.

From a practical point of view, the most important of these are *tremolite-asbestos* and *serpentine-asbestos*, which in the trade are known as 'Italian asbestos' and 'Canadian asbestos' respectively. The former is met with as aggregates or bundles of white or greyish fibres, sometimes several feet in length, usually arranged parallel to the surfaces of crevices in the metamorphic and crystalline rocks of mountainous districts. It is mined in the Alps, Urals, and Appalachians. The supply is limited and uncertain, and the hardness of the enclosing rocks makes mining difficult. The principal mines are those in the north of Italy, in the Susa and Aosta valleys in Piedmont, and the Valtellina in Lombardy.

Serpentine-asbestos, or chrysotile, occurs in small veins forming an irregular network in serpentine-rock. It has in the closely compacted mass an oil-yellow or greenish colour with a pronounced silky lustre and a certain degree of translucency. When rubbed or crushed, it readily separates into white cottony fibres (pierre à coton of the French-Canadians). The fibres are arranged perpendicularly to the walls of the vein, and are usually only an inch or two in length, never exceeding 6 inches. The mineral usually contains 2–3 p.c. FeO isomorphously replacing magnesia. Although chrysolite is found at all the localities where serpentine-rock occurs (*e.g.* the Lizard district in Cornwall), it is only in Canada that it is mined to any large extent, and there only since 1878. The mining districts are near the villages of Thetford, Black Lake, East Broughton, and Danville in Quebec. The asbestos quarried by the ancients at Karystos, in Eubœa (Karystian stone), and in Cyprus, was also a serpentine-asbestos (J. W. Evans, Mineral. Mag., 1906, xiv. 143). It was used for wicks in the perpetually burning lamps of the temples; and was woven into napkins, which could be cleansed by fire, and into cremation shrouds.

These two kinds of asbestos—the hornblende-asbestos and the serpentine-asbestos—differ somewhat in their resistance to acids and heat. Chrysotile is decomposed by hydrochloric and sulphuric acids; at a red heat (but not below) it loses water, and the fibres can be fused in the bunsen-flame. Tremolite-asbestos is not attacked by acids, and it is more difficultly fusible. (Crocidolite fuses readily to a black, magnetic glass.) On the other hand, the fibres of chrysotile are more flexible and more suitable for textile purposes. Notwithstanding these differences, the two varieties are put to the same uses, but serpentine asbestos is employed in far larger quantities. Spun asbestos is largely used for steam packings, fireproof curtains; and as cloth, twine, and rope it finds a variety of applications. As an insulating material, asbestos fibre is used for coating steam and hot-water pipes and cold-storage plants; and as a lining in safes, stoves, and furnaces. For use as a constructional fireproof material, it is made into bricks, boards, millboards, plasters, and paints, being often mixed with other materials. The so-called 'asbestic,' largely used for wall plaster, is prepared by grinding the poorer material and waste, which consists of narrow veins of asbestos still enclosed in the serpentine-rock. In the laboratory, asbestos is used for filtering (a pure white tremolite-asbestos being best for this purpose), for stoppings in combustion tubes, and in the form of card for supports. Asbestos paper or twine, soaked in sodium silicate and afterwards treated with calcium chloride solution, can be used for repairing glass apparatus.

The production of Canadian asbestos in 1908 amounted to 65,534 short tons (of 2000 lbs.), valued at about 510,000*l.*; and, in addition, 25,239 tons of 'asbestic,' valued at about 5000*l.* The prices per short ton vary from $150 to $350 (about 30*l.*–70*l.*) for the better qualities ('crude'), descending to $10 for the smaller material ('fibre' and 'paper stock').

References.—F. Cirkel, Asbestos, its Occurrence, Exploitation, and Uses (Mines Branch, Ottawa, 1905); R. H. Jones, Asbestos (London, 1890), and Asbestos and Asbestic (London, 1897); G. P. Merrill, Asbestos and other Asbestiform Minerals (Proc. U. S. Nat. Museum, 1895, xviii. 281), and 'Non-metallic Minerals' (New York, 1910); Production and Uses of Asbestos (Bull. Imp. Inst. 1905, iii, 277); The Technical Preparation of Asbestos, (*ibid.* 1908, vi. 393); J. S. Diller, Mineral Resources of the United States, for 1908, 1909, ii, 697; H. F. Olds, Blue Asbestos [Crocidolite in South Africa] (Trans. Inst. Mining and Metall. 1899, vii. 122). L. J. S.

ASDUANA *v.* BRIDELIA BARK.

ASEPTIN. Trade name for a mixture of hydrogen peroxide, boric acid, and salicylic acid, used as an antiseptic.

ASEPTOL. Trade name originally given to a solution of *o*-phenolsulphonic acid $C_6H_4(OH)SO_3H$. It is a thick reddish fluid, of 1·45 sp.gr., having a faint odour like phenol, occasionally called *sozolic acid*. It is an antiseptic, but does not possess the poisonous action peculiar to phenol, and is therefore recommended for surgical and ophthalmic operations (Chem. Zentr. 1884, 720).

The aseptol of Merck is *p*-phenol sulphonic acid mixed with about 6 p.c. of the *o*-acid (Obermiller, Chem. Zentr. 1907, 1615).

The name is also given to a preparation containing from 0·25 to 10 parts potassium oxyquinoline sulphate, 0·5 to 10 parts soap, dissolved in 1000 parts of water, mixed with terpineol or other aromatic substances, and occasionally glycerol (Pharm. Zeit. 1897, 770).

Aseptol is also the name given to an ill-defined mixture of phenyl ethers and sulphonated phenols, obtained by the action of sulphuric

acid on phenol in presence of alcohol (Trillat, J. Soc. Chem. Ind. 1892, 1028).

ASFRAX or *Trayamana*. An Indian drug, consisting of the flowers, flower-stalks, and immature fruit of a species of *Delphinium*. Used in Bombay as a medicine, and as a yellow dye for silk (Dymock, Pharm. J. [3] 8, 161).

ASH. This term is sometimes used to denote the inorganic or mineral matter contained in any substance, but more generally refers to the residue left on completely burning or incinerating it. The two meanings are not necessarily the same, since in any animal or vegetable substance the inorganic constituents are usually present in very different states of combination to those in which they occur in the residue left when the substance is completely oxidised.

To ascertain the exact amount and composition of the inorganic matter present in any organic substance is often a matter of considerable difficulty, and, in many cases, is impracticable.

The term 'ash' should be used, therefore, only in the second sense given above.

Most animal and vegetable substances leave, on combustion, a residue containing the following constituents in varying proportions :—

Acidic	Basic
Chlorine	Sodium
Carbon dioxide	Potassium
Sulphur trioxide	Calcium
Sulphur	Magnesium
Phosphorus pentoxide	Iron
Silica	Manganese

Other constituents, generally in small quantities, are also often present.

In the original substance the greater portions of the basic constituents in the above list are probably present in combination with organic acids, and, consequently, are left in the ash as carbonates (often largely the case with potash and soda) or as oxides (*e.g.* portions of the lime, magnesia, oxides of iron, and manganese); while the carbonates, sulphates, and phosphates are, in many cases, derived from organic combinations of carbon, sulphur, and phosphorus existing in the original substance. The determination of the amount and composition of the ash of animal and vegetable substances, though, perhaps, inadequate to ascertain the exact nature of the inorganic constituents of the organised bodies, affords valuable information as to their fitness as foodstuffs, and as to the needs of animals or plants.

In the process of incineration, there is great danger of loss of chlorides of potassium and sodium by volatilisation, also of reduction of phosphates and sulphates by the reducing action of the hot carbon. Berthelot proposed to overcome these difficulties by heating in a current of oxygen, the substance to be incinerated being previously mixed with a known weight of sodium carbonate (Compt. rend. 128, 23).

Shuttleworth (Chem. Zentr. 1899, ii. 144) has suggested the addition of calcium acetate in order to prevent the sintering which is so often an obstacle to complete incineration, and has devised a special platinum vessel in order to prevent loss of chlorides by volatilisation, and to hasten incineration. A modified form of this apparatus is described by Tucker (Ber. 32, 2583).

A convenient method of minimising the loss of chlorides by volatilisation is to char the substance thoroughly at a moderate temperature, then cool and extract the black residue with water, filter off the soluble matter, and complete the incineration of the residue after drying. When all black particles have disappeared, the residue is allowed to cool, the aqueous extract added, evaporated to dryness, and then moderately heated. Addition of ammonium nitrate to the black char hastens the combustion of the carbon.

Ash of animals. The proportion of ash constituents present in the whole body of an animal depends largely upon its condition, being greater in lean than in fat animals. According to the Rothamsted experiments, the following table gives the average proportions of ash and of its main constituents in the whole bodies of various farm animals in a fatted condition :—

—	Total ash	Phosphoric acid P_2O_5	Lime CaO	Magnesia MgO	Potash K_2O
Fat calf .	3·9	1·54	1·65	0·08	0·21
Half-fat ox .	5·1	1·84	2·11	0·09	0·21
Fat ox . .	4·2	1·55	1·79	0·06	0·18
Fat lamb .	3·2	1·13	1·28	0·05	0·17
Store sheep .	3·3	1·19	1·32	0·06	0·17
Fat sheep .	3·0	1·04	1·18	0·05	0·15
Store pig .	2·8	1·07	1·08	0·05	0·20
Fat pig .	1·7	0·65	0·64	0·03	0·14

The other constituents of the ash consist chiefly of sodium, chlorine, fluorine, iron, manganese, iodine, and silica.

The bones and teeth contain the greater part of the phosphoric acid, lime, magnesia, and fluorine; potash is present largely in muscle, blood, and many of the secretions; sodium, chlorine and iron are largely present in the blood and the secretions, while iodine is mainly accumulated in the thyroid gland.

(For the amount and composition of the ash of various portions of the animal body, and of certain animal products, *v.* BONES; BLOOD; MILK; &c.)

A characteristic of the ash of animal substances in general, is the usual preponderance of lime over phosphorus pentoxide, and the relatively high ratio of sodium to potassium.

Ash of plants. The nature of the ash of the leaves, stems, &c., of plants is affected to a considerable extent by the composition of the soil in which the plants grow, but the amount and composition of the ash of the *seeds* are much less variable.

In nearly all seeds the largest constituents of the ash are phosphorus pentoxide and potash. In certain seeds generally used in their husk, *e.g.* oats, millet, spelt, and barley, silica is a large constituent.

But in the leaves and stems of plants, phosphorus pentoxide usually forms but a small constituent of the ash, whilst potash and lime become relatively more abundant. In cereals and grasses, silica often forms more than half of the total ash of the straw and chaff.

The following table, compiled chiefly from Wolff's analyses, gives the average proportions of ash and of its chief components in various fresh or air-dried agricultural products.

100 parts of the substance contain:—

Substance	Water	Ash	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl	S
					I. *Green Fodder.*						
Meadow grass	70·0	2·33	0·60	0·16	0·11	0·27	0·15	0·12	0·69	0·19	0·06
Rye grass	70·0	2·13	0·53	0·09	0·05	0·16	0·17	0·08	0·84	0·11	0·07
Timothy grass	70·0	2·10	0·61	0·06	0·08	0·20	0·23	0·08	0·75	0·11	0·08
Oats, in blossom	77·0	1·66	0·65	0·06	0·05	0·11	0·14	0·05	0·55	0·07	0·04
Barley, „	68·0	2·25	0·59	0·01	0·07	0·14	0·22	0·07	1·08	0·08	0·07
Wheat, „	69·0	2·17	0·56	0·01	0·05	0·07	0·16	0·04	1·23	0·06	0·05
Rye fodder	70·0	1·63	0·63	0·01	0·05	0·12	0·24	0·02	0·52	—	—
Red clover	80·0	1·34	0·46	0·02	0·16	0·46	0·13	0·04	0·04	0·05	0·05
White clover	81·0	1·36	0·24	0·11	0·14	0·44	0·20	0·12	0·06	0·04	0·06
Lucerne	75·3	1·76	0·45	0·02	0·10	0·85	0·15	0·11	0·04	0·03	0·08
Sainfoin	78·5	1·16	0·46	0·02	0·07	0·37	0·12	0·04	0·05	0·03	—
Green vetches	82·0	1·57	0·66	0·05	0·11	0·41	0·20	0·06	0·03	0·05	0·03
Potato tops	77·0	1·18	0·07	0·01	0·27	0·55	0·06	0·06	0·05	0·04	0·05
Mangold tops	90·7	1·48	0·43	0·31	0·14	0·17	0·08	0·11	0·07	0·17	0·05
Sugar-beet tops	89·7	1·80	0·40	0·30	0·33	0·36	0·13	0·14	0·06	0·10	—
Turnip tops	89·8	1·40	0·32	0·11	0·06	0·45	0·13	0·14	0·05	0·12	0·05
Chicory tops	85·0	1·87	1·12	0·01	0·06	0·27	0·17	0·17	0·02	0·03	—
Carrot tops	80·8	2·61	0·37	0·60	0·12	0·86	0·12	0·21	0·15	0·19	0·14
Cabbage heads	88·5	1·24	0·60	0·05	0·04	0·19	0·20	0·11	0·01	0·03	0·05
Kohl-rabi tops	85·0	2·53	0·36	0·10	0·10	0·84	0·26	0·30	0·26	0·10	—
					II. *Hay and Straw.*						
Meadow hay	14·4	6·66	1·71	0·47	0·33	0·77	0·41	0·34	1·97	0·53	0·17
Red clover hay	16·0	5·65	1·95	0·09	0·69	1·92	0·56	0·17	0·15	0·21	0·21
White clover hay	16·0	6·03	1·06	0·47	0·60	1·94	0·85	0·53	0·27	0·19	0·27
Lucerne hay	16·0	6·00	1·52	0·07	0·35	2·88	0·51	0·37	0·12	0·11	0·26
Sainfoin hay	16·0	4·53	1·79	0·08	0·26	1·46	0·47	0·15	0·18	0·14	—
Oat hay	14·5	6·18	2·41	0·20	0·20	0·41	0·51	0·17	2·05	0·25	0·15
Wheat straw	14·1	4·26	0·49	0·12	0·11	0·26	0·23	0·12	2·82	—	0·16
Rye straw	15·4	4·07	0·76	0·13	0·13	0·31	0·19	0·08	2·37	—	0·09
Barley straw	14·0	4·39	0·93	0·20	0·11	0·33	0·19	0·16	2·36	—	0·13
Oat straw	14·1	4·40	0·97	0·23	0·18	0·36	0·18	0·15	2·11	—	0·17
Maize straw	14·0	4·72	1·66	0·05	0·26	0·50	0·38	0·25	1·79	—	0·39
Pea straw	14·3	4·92	1·07	0·26	0·38	1·86	0·38	0·28	0·28	0·30	0·07
Field bean straw	18·0	5·84	2·59	0·22	0·46	1·35	0·41	0·01	0·31	0·81	0·22
Buckwheat straw	16·0	5·17	2·41	0·11	0·19	0·95	0·61	0·27	0·28	0·40	—
Flax straw	14·0	3·19	1·18	0·16	0·23	0·83	0·43	0·20	0·22	0·15	0·14
Flax, whole plant	25·0	3·23	1·13	0·15	0·29	0·50	0·74	0·16	0·08	0·19	—
Hop, „ „	25·0	7·40	1·94	0·28	0·43	1·18	0·90	0·38	1·59	0·34	0·20
Hops	12·0	5·98	2·23	0·13	0·21	1·01	0·90	0·16	0·92	0·02	0·48
Tobacco	18·0	19·75	5·41	0·73	2·07	7·31	0·71	0·77	1·92	0·88	—
Heather	20·0	3·61	0·48	0·19	0·30	0·68	0·18	0·16	1·27	0·08	—
Broom	16·0	4·89	0·69	0·05	0·28	0·32	0·16	0·07	0·19	0·05	—
Fern	16·0	5·89	2·52	0·27	0·45	0·83	0·57	0·30	0·36	0·60	—
Reeds	18·0	3·85	0·33	0·01	0·05	0·23	0·08	0·11	2·75	—	—
Sedge	14·0	6·95	2·31	0·51	0·29	0·37	0·47	0·23	2·18	0·39	—
Rush	14·0	4·56	1·67	0·30	0·29	0·43	0·29	0·40	0·50	0·65	—
					III. *Root Crops.*						
Potato	75·0	0·94	0·56	0·01	0·04	0·02	0·18	0·06	0·02	0·03	0·02
Artichoke	80·0	1·03	0·67	—	0·03	0·04	0·16	0·03	—	0·02	—
Mangold	88·3	0·80	0·43	0·12	0·04	0·04	0·08	0·03	0·02	0·05	0·02
Sugar beet	81·6	0·80	0·40	0·08	0·07	0·05	0·11	0·04	0·03	0·02	—
Turnip	90·9	0·75	0·30	0·08	0·03	0·08	0·10	0·11	0·02	0·03	0·04
White turnip	91·5	0·61	0·31	0·02	0·02	0·08	0·11	0·04	0·01	0·04	—
Kohl-rabi	87·7	0·95	0·49	0·06	0·02	0·09	0·14	0·08	0·01	0·05	—
Carrot	86·0	0·88	0·32	0·19	0·05	0·09	0·11	0·06	0·02	0·03	0·01
Chicory	80·0	1·04	0·42	0·08	0·07	0·09	0·15	0·10	0·06	0·04	—

Substance	Water	Ash	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl	S
IV. *Grains and Seeds.*											
Wheat	14·3	1·77	0·55	0·06	0·22	0·06	0·82	0·04	0·03	—	0·15
Rye	14·9	1·73	0·54	0·03	0·19	0·05	0·82	0·04	0·03	—	0·17
Barley	14·5	2·18	0·48	0·06	0·18	0·05	0·72	0·05	0·59	—	0·14
Oats	14·0	2·64	0·42	0·10	0·18	0·10	0·55	0·04	1·23	—	0·17
Spelt	14·8	3·58	0·62	0·06	0·21	0·09	0·72	0·06	1·58	—	—
Maize	13·6	1·23	0·33	0·02	0·18	0·03	0·55	0·01	0·03	—	0·12
Sorghum	14·0	1·60	0·42	0·05	0·24	0·02	0·81	—	0·12	—	—
Millet	13·0	3·90	0·47	0·04	0·33	0·04	0·91	0·01	2·05	—	0·18
Paddy rice	12·0	6·90	1·27	0·31	0·59	0·35	3·26	0·04	0·04	—	—
Rice	13·0	0·34	0·08	0·02	0·05	0·01	0·17	—	0·01	—	—
Buckwheat	14·1	0·92	0·21	0·06	0·12	0·03	0·44	0·02	—	0·02	—
Flax seed	11·8	3·22	1·04	0·06	0·42	0·27	1·30	0·04	0·04	—	0·17
Peas	13·8	2·42	0·98	0·09	0·19	0·12	0·88	0·08	0·02	0·06	0·24
Field beans	14·1	2·96	1·20	0·04	0·20	0·15	1·16	0·15	0·04	0·08	0·23
V. *Fruits, &c.*											
Apple, whole fruit	84·0	0·27	0·10	0·07	0·02	0·01	0·04	0·02	0·01	—	—
Pear, „ „	80·0	0·41	0·22	0·04	0·02	0·03	0·06	0·02	0·01	—	—
Cherry, „ „	78·0	0·43	0·22	0·01	0·02	0·03	0·07	0·02	0·04	0·01	—
Plum, „ „	82·0	0·40	0·24	—	0·02	0·04	0·06	0·02	0·01	—	—
Acorns, fresh	56·0	0·96	0·62	0·01	0·05	0·07	0·16	0·05	0·02	0·01	—
Beech mast	18·0	2·71	0·62	0·27	0·31	0·67	0·56	0·06	0·05	0·01	—
Horse chestnuts	49·2	1·20	0·71	—	0·01	0·14	0·27	0·02	—	0·08	—
VI. *Leaves—Autumn.*											
Mulberry	67·0	1·17	0·23	—	0·06	0·30	0·12	0·01	0·41	—	—
Horse chestnut	60·0	3·01	0·59	—	0·24	1·22	0·25	0·05	0·42	0·12	—
Walnut	60·0	2·84	0·76	—	0·28	1·53	0·11	0·08	0·06	0·02	—
Beech	55·0	3·05	0·16	0·02	0·18	1·37	0·13	0·11	1·03	0·01	—
Oak	60·0	1·96	0·07	0·01	0·08	0·95	0·16	0·09	0·61	—	—
Scotch fir	55·0	0·63	0·06	—	0·06	0·26	0·13	0·03	0·08	0·03	—
Spruce	55·0	2·63	0·04	—	0·06	0·40	0·21	0·07	1·84	—	—
VII. *Manufactured Products.*											
Fine wheat flour	13·6	0·41	0·15	0·01	0·03	0·01	0·21	—	—	—	—
Wheat bran	13·5	5·56	1·33	0·03	0·94	0·26	2·88	—	0·06	—	—
Rye flour	14·2	1·69	0·65	0·03	0·14	0·02	0·85	—	—	—	—
Rye bran	13·1	7·14	1·93	0·09	1·13	0·25	3·42	—	—	—	—
Barley flour	14·0	2·00	0·58	0·05	0·27	0·06	0·95	0·06	—	—	—
Maize meal	14·0	0·95	0·27	0·03	0·14	0·06	0·43	—	—	—	—
Malt	4·2	2·66	0·46	—	0·22	0·10	1·07	—	0·88	—	—
Malt dust	9·2	5·96	2·08	—	0·08	0·09	1·25	0·38	1·77	—	—
Beer	90·0	0·39	0·15	0·03	0·02	0·01	0·13	0·01	0·04	0·01	—
Wine	86·6	0·28	0·18	—	0·02	0·02	0·05	0·01	0·01	—	—
Linseed cake	11·5	5·52	1·29	0·08	0·88	0·47	1·94	0·19	0·36	0·03	—
Cotton-seed cake	11·5	6·15	2·18	—	0·26	0·28	2·95	0·07	0·25	—	—
Potato skins	30·0	6·71	4·83	0·05	0·45	0·64	0·23	0·03	0·18	0·14	—
Buckwheat groats	14·0	0·62	0·16	0·04	0·08	0·01	0·30	0·01	—	0·01	—
VIII. *Wood (air-dried).*											
Apple tree	15·0	1·10	0·13	0·02	0·06	0·78	0·05	0·03	0·02	—	—
Beech, trunk	15·0	0·55	0·09	0·02	0·06	0·31	0·03	0·01	0·03	—	—
Beech, brushwood	15·0	1·23	0·17	0·03	0·13	0·59	0·15	0·01	0·12	—	—
Birch	15·0	0·26	0·03	0·02	0·02	0·15	0·02	—	0·01	—	—
Grape	15·0	2·34	0·70	0·16	0·16	0·87	0·30	0·06	0·02	0·02	—
Mulberry	15·0	1·37	0·09	0·20	0·08	0·78	0·03	0·14	0·05	0·06	—
Larch	15·0	0·27	0·04	0·02	0·07	0·07	0·01	0·01	0·01	—	—
Oak	15·0	0·51	0·05	0·02	0·02	0·37	0·03	0·01	0·01	—	—
Scotch fir	15·0	0·26	0·03	0·01	0·02	0·13	0·02	0·01	0·04	—	—

In addition to the constituents given in the above table, small quantities of oxides of iron and manganese are almost invariably present in vegetable ashes.

Titanium (Wait, J. Amer. Chem. Soc. 1896, 18, 402), aluminium, fluorine, and boron (Crampton, Amer. Chem. J. 11, 227; Jay, Compt. rend. 121, 893; Baumert, Ber. 21, 3290), are also frequently present in small quantities in the ash of certain plants.

Lithium, rubidium, zinc, copper, barium, and arsenic have also been detected in the ash of certain plants grown in soils containing these constituents (Passerini, Chem. Soc. Abstr. 1893, ii. 225; Homberger, *ibid.* 1899, A, ii. 506; Macdougal, *ibid.* 1900, A, ii. 235).

Even chromium, molybdenum, and vanadium have been detected in the ash of fir, oak, vine, and poplar (Demarcay, *ibid.* 1900, 235).

Indeed, the composition of the soil has a great influence upon the amount and composition of the ash of the crop grown upon it, though this influence is much more marked upon the foliage, stem, &c., than upon the seed.

Certain plants, originating from plants of the seashore, *e.g.* asparagus, beet, and carrot, generally leave an ash containing unusually high amounts of chlorine and sodium, and application of common salt as manure to such crops is usually stated to be beneficial, although on no very sufficient evidence.

Plants like salt-worts (*Salsola*) and samphire (*Salicornia*) growing on the coast, contain relatively enormous quantities of soda—in the former 6 times, in the latter 14 times, as much soda as of potash.

The ash of the club-moss (*Lycopodium*) contains from 20 to 50 p.c. of alumina.

As already stated, some of the phosphates and sulphates found in the ash of plants result from the oxidation of phosphorus and sulphur organic compounds present in the original plant.

Posternak (Compt. rend. 137, 1903) detected the existence in peas, beans, potatoes, and the seeds of the red fir, pumpkin, white and yellow lupines of *anhydro-oxymethylene diphosphoric acid*—

$$O\begin{<}CH_2—OPO(OH)_2\\CH_2—OPO(OH)_2\end{>}$$

Patten and Hart (Bull. 250 (1904), N. York Agric. Expt. Station) have shown that about 86 p.c. of the total phosphorus in bran, 81 p.c. in malt sprouts, and 50 p.c. in oats, is soluble in 0·2 p.c. sol. of hydrochloric acid; and that the greater portion of this is present in the bran as calcium, magnesium and potassium salts of anhydro-oxymethylene diphosphoric acid.

Importance of the Ash Constituents of Foods.

The influence of the mineral matter in the food of animals upon their health and well-being is probably much greater than is generally recognised. Not only is it essential that all the inorganic constituents required for building up the tissues and producing the various digestive and other secretions be supplied in sufficient quantities, but it is important, at least with certain pairs of constituents, that they be supplied in appropriate ratios to each other.

A preponderance of phosphoric acid over lime and magnesia in the diet is probably the cause or a predisposing cause of certain diseases of the bones of horses, mules, and donkeys (Ingle, Jour. Comp. Pathology and Therapeutics, 1907; Jour. Agric. Science, 1908, iii. 22; Jour. Roy. Inst. Public Health, 1909); while the ratio of potash to soda in the food has an important bearing upon health, and especially upon the susceptibility to certain diseases, *e.g.* scurvy.

The cereals contain a large excess of phosphoric acid over lime, and the use of an exclusively cereal diet may lead to imperfect bone nutrition (*l.c.*; also Illustrated Poultry Record, 1910).

The necessity of an adequate supply of chlorides in the diet is well recognised, and in many countries the ordinary food supplies of domestic animals have to be supplemented by common salt to ensure healthy existence.

Whenever the rations are restricted to one or two items, there is considerable probability that certain mineral constituents will be lacking or supplied in improper proportions.

It is too often the practice, in discussing the feeding of animals, to devote much consideration to the organic portions of their food, but beyond requiring that sufficient mineral matter or '*bone-forming*' material be present, to pay little or no attention to its composition.

Thus bran is widely regarded as a food particularly rich in mineral matter, and therefore valuable for bone nutrition; but the ratio of phosphorus pentoxide to lime in this food is about 11 to 1, and the practice of feeding animals largely upon bran is known to produce a disease of the bones—'bran rachitis' in horses.

Kellner (Scientific Feeding of Animals, 1909) estimates that for oxen, 50 grams of phosphorus pentoxide and 100 grams of lime per 1000 kilos. body weight per day, are required in the food, while for full-grown sheep, 1 gram of the former and 11 grams of lime suffice.

In England, fortunately, hay—either meadow or clover—forms a large part of the rations of farm animals, and this contains a large excess of lime over phosphoric acid, and thus neutralises the opposite preponderance in the grain or cake used with it.

But in South Africa and perhaps some other countries, meadow or clover hay is but little used, and many horses are fed entirely upon oat hay or oat hay and maize. In either case there is a large preponderance of phosphoric acid over lime, and to this fact the prevalence of certain bone diseases is almost certainly due.

Similar considerations apply to other animals kept in confinement, especially to poultry when deprived of a grass run, and to pigs. H. I.

ASPARAGINE. *Aminosuccinamic acid* $C_2H_3{\cdot}NH_2(CO_2H)(CO{\cdot}NH_2)$ occurs in two optically active forms, differing in direction of rotatory power and in taste. *Lævo-asparagine*, discovered by Vauquelin and Robiquet (Ann. Chim. anal. 1805, 57, 88) in the young shoots of asparagus (*Asparagus officinalis*, Linn.), is widely distributed in the vegetable kingdom, occurring in most plants at the time of budding and during the flowering period, and, with glutamine, forms the chief non-proteid compounds present in the juice of ripening oranges (Scurti and de Plato, Chem. Zentr. 1908, ii. 16, 1370). Miyacha (Bull. Coll. Agric. Imp. Univ. Tokyo, 1897, 2, 458) has shown that in the cases of *Pœonia albiflora* and *Thea chinensis*, even old leaves, showing incipient decay, can produce asparagine. It occurs to a larger extent in leguminous plants than in any other natural order, and is most abundant at the time of germination, the quantity being greater in etiolated than in normal plants (Borodin, Bied. Zentr. 1879, 357),

Sachsse (Landsw. Versuchs. Stat. 1874, 17, 88) found that the amount of asparagine in germinating peas increased from 0·67 to 6·94 p.c. during 24 days' growth; and Schulze and Umlauft (*ibid.* 1875, 18, 1) found 17·9 p.c. of asparagine in the dried shoots of *Lupinus luteus* seedlings germinated in the dark in distilled water (compare also Mercadante, Gazz. ital. chim. 1875, 5, 187; Schulze, Landsw. Versuchs. Stat. 1895, 46, 383; Stoklasa, Landw. Jahrb. 1895, 24, 827; Bourquelot and Herissey, J. Pharm. 1898, (vi.) 8, 385; Bréal, Ann. Agron. 1900, 26, 5; Schulze and Barbieri, Landsw. Versuchs. Stat. 21, 63; Kinoshita, Bull. Coll. Agric. Imp. Univ. Tokyo, 1895, 2, 203); Schulze and Bosshard, Zeitsch. physiol. Chem. 1885, 9, 420; Bungener, Bied. Zentr. 1885, 861; Behrens, Bot. Zentr. 1894, 178). Asparagine is one of the decomposition products of proteid matter (Schulze, Bied. Zentr. 1901, 30, 106; Chem. Zentr. 1901, i. 1108; Ber. Deut. Bot. Ges. 1907, 25, 213), and its accumulation in the plant during the periods of germination and budding, particularly when the development occurs in the dark is attributed by Borodin (Bied. Zentr. 1879, 357) and Schulze and Barbieri (J. pr. Chem. 1882, [2] 25, 145), to the absence of carbohydrates which under conditions of normal assimilation effect the reincorporation of amides into proteid molecules; and this view is confirmed by Monteverde (Ann. Agron. 17, 376), who found that branches of lilac plunged in distilled water or 4 p.c. glycerol solution and kept in the dark, contained abundance of asparagine at the end of 15 days, but neither starch nor mannitol. When, however, branches of the same plant were kept in solutions of glucose, sucrose, or mannitol, they formed no asparagine in a month, but contained much mannitol and starch. Another source of asparagine in the plant is its synthetic formation from ammonium salts, urea, or nitrates supplied by the soil. This synthetic production is only possible in the presence of sugar, and under conditions that exclude the formation of proteids (Suzuki, Bull. Coll. Agric. Imp. Univ. Tokyo, 1895, 2, 196). The function of the asparagine in the plant economy is the production of proteid matter; hence the addition of leguminous seeds after steaming to the mash in brewing is recommended by Birner (J. Soc. Chem. Ind. 1882, 333), as the asparagine they yield forms excellent nutriment for the yeast cell; and Kinoshita (Bull. Coll. Agric. Imp. Univ. Tohyo, 1895, 2, 196) found that young shoots of soja bean that showed an increase in asparagine, from 21·5 to 28·7 p.c. after four weeks' natural growth, became poorer in asparagine (18·9–13·7 p.c.) if grown for the same period in methyl alcohol and glycerol solution, but contained reserve proteid matter.

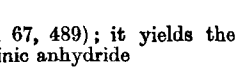
Asparagine can be extracted from the juice expressed from young vetch seedlings that have germinated in the dark, 10 kilos. of vetch yielding 150 grams of pure asparagine (Piria, Annalen, 1848, 68, 343).

Asparagine crystallises from aqueous solution in large rhombic lævo- hemihedral prisms, $a:b:c::0{\cdot}4752:1:0{\cdot}8294$ (Freundler, Compt. rend. 1897, 125, 657), containing $1H_2O$, which it loses at 100°, and then melts at 234°–235° (Michael, Ber. 1895, 28, 1629); it has a sp.gr. 1·5434 at 14·8°/4° (Piutti, Gazz. ital. chim. 1904, 34, 36); the molecular heat of combustion is 448·4 Cals., and the heat of formation 205·1 Cals. (Berthelot and Andre, Compt. rend. 1890, 120, 884); it is sparingly soluble in cold, readily so in hot water—1 part dissolves in 82 parts of water at 10°, in 47 parts at 20° (Becker, Ber. 1881, 14, 1028), in 58 parts at 13°, and 1·89 parts at 100° (Guareschi, Gazz. chim. ital. 1876, 6, 370; compare Bresler, Zeitsch. physikal. Chem. 1904, 47, 611). The aqueous solution is weakly acid, has an insipid and disagreeable taste, and is lævo-rotatory $[\alpha]_D - 5°\ 4'$ (Piutti, Compt. rend. 1886, 103, 134); the rotatory power of the solution is increased by the addition of alkalis, inverted by mineral acids, and destroyed by acetic acid (Champion and Pellet, Compt. rend. 1876, 82, 819; Becker, Ber. 1881, 14, 1028). Advantage is taken of this last fact to eliminate the error due to the presence of asparagine in saccharimetric determinations of sugar liquors from beets and canes. Asparagine is partially hydrolysed by boiling with water, forming *aspartic acid* (*aminosuccinic acid*) $C_2H_3{\cdot}NH_2(CO_2H)_2$ and ammonia; the change is rapid and complete when excess of barium hydroxide or dilute hydrochloric or sulphuric acid is employed (Schulze, Landsw. Versuchs. Stat. 29, 233); by the action of potassium permanganate, asparagine is oxidised to carbamide and ammonia; and when used in 5 p.c. aqueous solution for the culture of *Bacillus pyrocyanicus*, it is converted into aspartic acid after 60 hours, and completely decomposed after 72 hours (Arnaud and Charrin, Compt. rend. 1891, 112, 755; Adeney, Proc. Roy. Irish Acad. 1905, 25, 6). Under the action of enzymes, asparagine yields a mixture of formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Zeitsch. 1909, 18, 424), and a similar change is effected by brewer's yeast (Effront, Mon. Sci. 1909, (iv.) 23, i. 145).

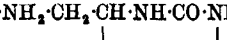
The estimation of asparagine is based upon its quantitative conversion into aspartic acid and ammonia by the action of hydrochloric acid, the aspartic acid may be removed in the form of its sparingly soluble copper salt (Engel, Compt. rend. 1888, 106, 1734) and the ammonia determined by Sachsse's method (J. pr. Chem. 1872, [2] 6, 118) or by one of the modifications of Schloessing's method described by Meunier (Ann. Agron. 6, 275), by Schulze (J. pr. Chem. 1885, [2] 31, 233), or by Brown and Millar (Jour. Soc. Chem. Ind. 1904, 135).

Asparagine has feeble basic and acidic properties, and forms salts with acids and bases (Chautard and Dessaigne, Annalen, 1848, 68, 349; Dessaigne, Annalen, 1852, 82, 237; Smolka, Monatsh. 1887, 6, 915); it also forms double compounds with certain salts of the heavy metals, the sparing solubility of the compound with mercuric nitrate is made use of in isolating small quantities of asparagine from solutions containing carbohydrates (Schulze, Ber. 1882, 15, 2855); the *alum* $(C_4H_8O_3N_2)_2H_2SO_4Al_2(SO_4)_3{,}24H_2O$ forms octahedral crystals. Asparagine is converted into *l*-chlorosuccinic acid and fumaric acid by the action of nitrosyl chloride in hydrochloric acid solution (Tilden and Forster, Chem. Soc.

Trans. 1895, 67, 489); it yields the amide of uramidosuccinic anhydride



when fused with carbamide (Guareschi, Gazz. ital. chim. 1876, 6, 370), and is converted into amidosuccinuric acid



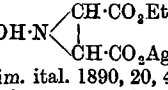
m.p. 137°–138°, by the action of potassium cyanate (Guareschi, Ber. 1877, 10, 1747). Certain condensation products of asparagine with other amino- acids are described by Fischer (Ber. 1904, 37, 4585; 1907, 40, 2048), *chloroacetylasparagine*, m.p. 148°–149° (corr.); *glycylasparagine*, m.p. 216°, $[\alpha]_D$ −6·4° at 20°; *anhydroglycylasparagine*, decomposing at 274°; *d-leucyl-l-asparagine*, decomposing at 230° (corr.), $[\alpha]_D$ −53·6° at 20°; *l-leucyl-d-asparagine*, m.p. 228° (corr.), $[\alpha]_D$ +17·8°; *asparagylaspartic acid*, decomposing at 120°. Sasaki (Beitr. Chem. Physiol. Path. 1907, 10, 120) describes a *benzoylpolypeptide* of asparagine $C_{19}H_{24}O_8N_6$, decomposing at 210°, and giving the biuret reation.

As regards the alimentary value of asparagine, it has been found that in the case of herbivorous mammals and geese, asparagine has a proteid-sparing action, and under appropriate conditions prevents waste and causes the formation of proteid matter (Weiske, Bied. Zentr. 1879, 744; 1882, 312; Zeit. für Biol. 15, 261; 20, 276; Landws. Versuchs. Stat. 1888, 34, 303; Rosenfeld, Zeit. Ver. Deutsch. Zucker. Ind. 1900, [539] 1055, from Jour. Soc. Chem. Ind. 1901, 271). According to Zuntz and Müller (Pflüger's Archiv. 1906, 112, 245), the proteid-sparing action of asparagine is the result of a kind of symbiosis, the bacteria in the paunch of the ruminants decomposing the asparagine in preference to the protein in the food. In the case of omnivora and carnivora, asparagine exerts only a diuretic action (Murck and Voit, Bied. Zentr. 1884, 749; Politis, Zeit. Biol. 1893, 27, 492; Mauthner, *ibid.* 507; Gabriel and Voit, *ibid.* 29, 115, 125; Levena and Kohn, Amer. Jour. Physiol. 1909, 23, 324).

Dextro-asparagine was discovered by Piutti (Ber. 1886, 19, 1691) in the young shoots of the vetch (*Vicia sativa*, Linn.) 6500 kilos. of vetch buds yielded 20 kilos. of crude asparagine, from which 100 grams of pure dextro-asparagine was isolated; it is slightly more soluble than the lævo- compound; the solution has an intensely sweet taste, is dextro-rotatory in neutral or alkaline solution $[\alpha]_D$ +5·41° (Piutti, Compt. rend. 1886, 103, 134), and lævo-rotatory in acid solution; it forms large rhombic dextro-hemihedral crystals, $a:b:c::0{\cdot}4741:1:0{\cdot}8310$ (Freundler, Compt. rend. 1897, 125, 657). A solution of equal parts of the two optically active asparagines is optically inactive, but the two varieties separate on crystallisation, twining frequently taking place between the left and right crystals (Piutti, Compt. rend. 1886, 103, 134).

According to Pringsheim (Zeitsch. physiol. Chem. 1910, 65, 89), the *d*-asparagine found by Piutti is the mother liquors from which the *l*-asparagine had been isolated, was formed by the racemisation of the *l*-asparagine during the process of evaporation of the solutions. The author states that after boiling *l*-asparagine [$[\alpha]_D^{20}$ +36·19°, in *N*/10 hydrochloric acid solution] for 12 hours, with water, and subsequent fractional crystallisation, he obtained a fraction that had $[\alpha]_D^{20}$ −15·3° in *N*/10 hydrochloric acid solution, and therefore contained *d*-asparagine.

In addition to the two asparagines already described, there is a third form known as *α*-asparagine; it does not occur naturally; is optically inactive, crystallises in the triclinic system, $a:b:c=1{\cdot}5957:1:0{\cdot}5668$; $\alpha=91°19'$; $\beta=113°/12'$, $\gamma=83°\ 48'$ (Brugnatelli); and has a sp.gr. 1·454 at 14·8°/4° (Piutti, Gazz. chim. ital. 1904, 34, ii. 36), and is not structurally identical with the optically active or *β*-asparagines. The three asparagines have been synthesised by Piutti (Gazz. chim. ital. 1887, 17, 126; 1888, 18, 457) by the following methods, that leave no doubt as to the constitution of the compounds. By the reduction of the oxime of oxalacetic ester $CO_2Et{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$ with sodium amalgam and partial saponification of the product, Piutti obtained two different ethyl hydrogen aspartates, melting at 165° and 200° respectively. The ester melting at 165° is identical with the compound obtained by reducing Ebert's (Annalen, 1885, 229, 45) monoethyl ester of oximinosuccinic acid, which has the formula $CO_2H{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$, since on heating it loses CO_2 and forms oximinopropionic ester $CH_3{\cdot}C(NOH){\cdot}CO_2Et$. It follows, therefore, that the ethyl hydrogen aspartate melting at 165° is the monoethyl *α*-aspartate $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2Et$, and the ester melting at 200° must be the monoethyl *β*-aspartate $CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CO_2Et$. When these esters are treated with alcoholic ammonia, they are converted into the corresponding asparagines; the ester m.p. 165° gives inactive *α-asparagine* $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CONH_2$, and the ester m.p. 200° yields a mixture of *d*- and *l*- *β*-asparagines $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CONH_2$. From silver ethyl *γ*-oximinosuccinate



Piutti (Gazz. chim. ital. 1890, 20, 402) obtained a mixture of the three asparagines, the *α*-asparagine readily gave up its water of crystallisation in a vacuum, and fell to powder; and the *d*- and *l*- *β*-asparagines could then be separated by hand sorting. A mixture of the three asparagines was also obtained by the action of alcoholic ammonia on the ethyl hydrogen ester of inactive aspartic acid (Piutti, Gazz. ital. chim. 1887, 17, 126; 1888, 18, 457). Körner and Menozzi (Gazz. ital. chim. 1887, 17, 171, 226) effected the synthesis of the *d*- and *l*- *β*-asparagines from ethyl bromosuccinate, from ethyl fumarate or ethyl maleate, by the action of alcoholic ammonia; and similar results were obtained by Piutti (Ber. 1896, 29, 2069) with *l*-bromosuccinamic acid or maleic anhydride.

β-Ethylasparagine $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NHEt$, m.p. 258°–260°, with decomposition, and *β-allylasparagine* $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_3H_4$, melting and decomposing at 258°–261°, prepared by the action of the corresponding alkylamine on *β*-ethylaspartic acid,

yield optically inactive solutions (Piutti, Gazz. chim. ital. 1888, 18, 478). M. A. W.

ASPARAGUS. The shoots of this plant (*Asparagus officinalis*) are used as a table vegetable.

	Water	Protein	Fat	Carbohydrates	Ash
Average composition	94·0	1·8	0·2	3·3	0·7

The nitrogenous matter of asparagus consists largely of *amino-succinamic acid* $CO(NH_2)\cdot CH_2\cdot CH(NH_2)\cdot COOH$, a substance known (from its discovery, in 1805, in asparagus shoots) as *asparagine* (*q.v.*).

Coniferin and vanillin have also been found in the sap and cellular tissue (Lippmann, Ber. 1886, 18, 3355); Tanret (Compt. rend. 1909, 149, 48) describes two new carbohydrates as occurring in approximately equal quantities in asparagus roots—*asparagose* $(C_6H_{10}O_5)_n\cdot H_2O$, where $n=15$ or 16, crystallising in microscopic needles, soluble in water, insoluble in absolute alcohol, m.p. 198°–200°, gives no colouration with iodine, and does not reduce Fehling's solution; and *ψ-asparagose*, a white, hygroscopic substance more soluble than asparagose. Both substances are hydrolysed by invertase, yielding dextrose and lævulose.

The seeds of asparagus were examined by Peters (Arch. Pharm. 1902, 240, 53), and were found to contain water 11·5, woody fibre 8·2, nitrogen 3·0, and oil 15·3 p.c. Starch was not present, but a reserve cellulose (mannan), capable of yielding *d*-mannose on boiling with dilute hydrochloric acid, occurred; 37·5 p.c. of the weight of the seeds, of mannose was obtained. The oil was reddish yellow, had a sp.gr. of 0·928 at 15°, and an iodine number of 137·1. H. I.

ASPARTIC ACID. *Aminosuccinic acid* $CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, found in young sugar cane and in molasses of sugar beet (Scheibler, J. 1886, 399), and in young shoots of the gourd (Schulze and Barbieri, Ber. 1878, 11, 710), has been observed in diseased liver (Taylor, Zeitsch. physiol. Chem. 1901, 34, 580), and occurs in certain glands of *Tritonium nodosum*, the posterior portion of the gland when stimulated secretes an acid fluid from which aspartic acid immediately crystallises. As aspartic acid is soluble in sea-water, it is probably employed by the animal in destroying the calcareous shells of the other shellfish that form its food (Henze, Ber. 1901, 34, 348).

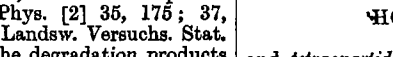
Aspartic acid is prepared by hydrolysing asparagine by means of hydrochloric or sulphuric acid, lime, baryta, lead oxide or potash (Plisson, Ann. Chim. Phys. [2] 35, 175; 37, 81; 40, 303; Schulze, Landsw. Versuchs. Stat. 29, 233); it is one of the degradation products of proteid matter, and is obtained when casein or proteid is heated with (1) dilute sulphuric acid (Kreussler, J. pr. Chem. 1869, 107, 239; Ritthausen, *ibid.* 218; Fischer, Zeitsch. physiol. Chem. 1901, 33, 151; 1902, 35, 70; 36, 462); (2) bromine or with stannous chloride (Hlasiwetz and Habermann, Annalen, 1871, 159, 325; 1873, 169, 162). Aspartic acid is produced by the oxidation of conglutin with potassium permanganate (Pott, J. pr. Chem. 1873, [2] 6, 91), by the pancreatic digestion of fresh blood fibrin at 40°–50° (Radziejewski and Salkowski, Ber. 1874, 7, 1050), or of gluten (Knieriem, Zeitsch. f. Biol 1876, 11, 198); and is one of the acid constituents of Kühne's 'antipeptone' (Kutscher, Zeitsch. physiol. Chem. 1898, 25, 195; 26, 110).

The naturally occurring aspartic acid is lævo-rotatory and the same *l-aspartic acid* is obtained by hydrolysis of *lævo*-asparagine (Schiff, Ber. 1884, 17, 2929); it crystallises in rhombic prisms, m.p. 270°–271° (Michael, Ber. 1895, 28, 1629), is sparingly soluble in water, 100 grams of water dissolve y mg. of the acid at $t°$, where

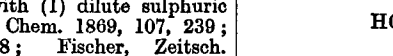
$$y=372+14\cdot1t-0\cdot18124t^2+0\cdot0053t^3$$

(Engel, Compt. rend. 1888, 106, 1734). A solution containing 1·873 p.c. of acid is feebly dextro-rotatory below 75°, but lævo-rotatory above that temperature; in alkaline solutions the substance is strongly lævo-, and in acids strongly dextro-, rotatory (Becker, Ber. 1881, 14, 1028). The heat of combustion is 387·2 Cals., the heat of formation 231·9 Cals. (Berthelot and André, Compt. rend. 1890, 110, 884); the heat of dissolution at 16° is −7·25 Cals., heat of neutralisation by sodium hydroxide +3·0 Cals. for the first, and +3·5 Cals. for the second equivalent (Berthelot, Compt. rend. 1891, 112, 829). Aspartic acid is readily soluble in aqueous solutions of certain mineral salts; for this reason Schiff (Ber. 1886, 17, 2929) recommends that in its preparation from asparagine by boiling with hydrochloric acid, the minimum quantity (2 mols.) of acid be employed, and the excess afterwards neutralised by ammonia (1 mol.); by adopting this precaution, a yield of 90 p.c. of the theoretical is obtained.

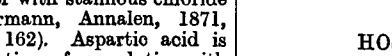
Aspartic acid forms salts with acid and bases, the copper salt $C_4H_5O_4NCu,4\frac{1}{2}H_2O$, forms pale-blue needles almost insoluble in cold water (Engel, *l.c.*). Aspartic acid is oxidised by hydrogen peroxide to the semi-aldehyde of malonic acid which breaks up into acetaldehyde and carbon dioxide (Dakin, Jour. Biol. Chem. 1909, 5, 409); it is capable of furnishing the nitrogeen required for the development of *B-coli communis* in presence of mannitol and glucose, becoming reduced to ammonium succinate (Harden, Chem. Soc. Trans. 1901, 623), and by enzyme action it is decomposed into formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Zeitsch. 1909, 18, 424; Borchardt, Zeitsch. physiol. Chem. 1909, 59, 96). When aspartic acid is heated at 190°–200° for 20 hours, and the product boiled with water, two sparingly soluble anhydrides, *octoaspartide*



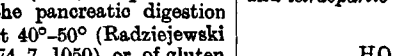
and *tetraspartide*



are obtained, the more soluble *octoaspartic*



and *tetraspartic acid*



can be isolated from the filtrate (Schiff, Ber. 1897, 30, 2449). The following alkyl esters of aspartic acid are described: *Monoethyl asparate hydrochloride*, m.p. 199°; *diethyl* and *dimethyl aspartate hydrochlorides*, deliquescent solids (Curtius and Koch, Ber. 1885, 18, 1293; Wegscheiden and Frankl, Monatsh. 1906, 27, 487), *ethyl β-aspartate* $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2Et$, m.p. 200°; *ethyl α-aspartate* $CO_2H{\cdot}CH_2{\cdot}CH(NH_2)CO_2Et$, m.p. 165° (Piutti, Chem. Zentr. 1888, 1459). The methyl, ethyl, allyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl hydrogen esters are dextro-rotatory at ordinary and lævo-rotatory at higher temperatures, and form sparingly soluble copper salts (Piutti and Maghi, Gazz. chim. ital. 1906, 36, ii. 738). *l*-Diethylaspartate has b.p. 126·5°/11 mm. pressure; sp.gr. 1·089 at 17° and $[\alpha]_D^{20°} = -9·46°$ (Fischer, Sitzungber, Akad. Wiss. Berlin, 1900, 48, 1062), or b.p. 126°–127°/10 mm., 150°–152°/25 mm. pressure, and forms a yellow *picrolonate* $C_9H_{15}O_4N,C_{10}H_8O_5N_4$, m.p. 290° (Schmidt and Widman, Ber. 1909, 42, 497).

Of the *acyl* derivatives of aspartic acid, the *benzenesulphonyl* derivative $SO_2Ph{\cdot}NH{\cdot}C_2H_3(CO_2H)_2$ melts at 170° (Hedin, Ber. 1891, 23, 3196); the *hippuryl* derivative $NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_2H_3(CO_2H)_2$, m.p. 191° (Curtius and Curtius, J. pr. Chem. 1904; (ii.) 70, 158); *benzoyl l-aspartic acid*, m.p. 184°–185° (corr.); has $[\alpha]_D^{20°} + 37·4°$, *leucyl aspartic acid* $CH_2Pr^{\beta}{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}C_2H_3(CO_2H)_2,H_2O$ decomposes at 180°–182° (corr.) (Fischer and Koenigs, Ber. 1904, 37, 4585); and the *picryl* derivative $C_{10}H_8O_{10}N_4$ has m.p. 137°; *aspartic diamide* $C_2H_3(NH_2)(CONH_2)_2$, m.p. 131°, has $[\alpha]_D - 7°$, and gives the biuret reaction (Fischer and Koenigs, Ber. 1904, 37, 4585). Aspartic acid resembles asparagine in its physiological action (Salkowski, Zeitsch. physiol. Chem. 1904, 42, 1207; Andrlík and Velich, Zeitsch. Zuckerind. Böhn, 1908, 32, 313).

d-Aspartic acid, obtained by hydrolysis of *d*-asparagine (Piutti, Ber. 1886, 19, 1694), or from *l*-bromosuccinic acid and aqueous ammonia at −40°, a Walden rearrangement taking place (Fischer and Raske, Ber. 1907, 40, 1051); is also obtained from a solution of the racemic acid [(*d*+*l*) aspartic acid] which has been inoculated with a mould grown on *l*-aspartic acid (Engel, Compt. rend. 1887, 106, 1734). *Benzoyl d-aspartic acid*, obtained by Fischer (Ber. 1899, 32, 2451), by the resolution of the racemic compound, through the brucine salts, has m.p. 181°–182°, $[\alpha]_D^{20°} - 37·6°$ in alkaline solution.

Inactive, *(d+l)-aspartic acid*, prepared by the action of boiling hydrochloric or nitric acid on the product obtained by heating the ammonium salts of malic, maleïc, or fumaric acids (Dessaigne, Compt. rend. 1850, 30, 324); by heating an aqueous solution of the hydrochloride of *l*-aspartic acid at 170°–180° for some hours (Michael and Wing, Ber. 1884, [1] 2984); by heating *d*- or *l*-aspartic acid with 2 mols. HCl (sp.gr. 1·107) at 170°–180°, or from an aqueous solution of equal parts of the *d*- and *l*- acids; the racemic acid crystallises out (Piutti, Ber. 1886, 19, 1694); by reducing and hydrolysing the sodium salt of ethyl oximino-oxalacetate (Piutti, Chem. Zentr. 1888, 68). (*d* + *l*)-Aspartic acid forms small monoclinic prisms; 100 grams of water dissolve *y* mg. of the acid at *t*°, where

$$y = 517 + 21·693t - 0·165t^2 + 0·0079t^3$$

(Engel, Compt. rend. 1888, 106, 1734). The copper salt $CuC_4H_5O_4N,4\frac{1}{2}H_2O$ is dark-blue (Engel. *l.c.*). The *benzoyl* derivative has m.p. 164°–165° (corr.), and can be resolved into its active components by crystallising the brucine salt (Fischer, Ber. 1899, 32, 2451).

M. A. W.

ASPHALT. *Compact bitumen, Mineral pitch, Jews' pitch, Bitumen of Judæa.* (*Judenpech, Erdpech, Bergpech*, Ger.; *Goudron minéral*, Fr.) A name given to the solid varieties of bitumen. In its purest form asphalt presents the appearance of a black or brownish-black solid substance, possessing a bright conchoidal fracture. It melts at 100°, burning with a brilliant flame and emitting a bituminous odour. Sp.gr. 1·0–1·68. Asphalt is insoluble in alcohol and water, soluble in about five times its weight of naphtha, and in benzol. It is dissolved by alkalis and alkaline carbonates.

By dry distillation a yellow oil, **Asphalt oil**, is obtained. It consists of hydrocarbons mixed with a small quantity of oxidised matter. It begins to boil at 90°, but the boiling-point gradually rises to 250°. The portion boiling below 200° has the sp.gr. 0·817 at 15°; that above 200° has a sp.gr. of 0·868 at 15°. Both portions gave by analysis about 87·5 p.c. carbon, 11·6 p.c. hydrogen, and 0·9 p.c. oxygen, which is nearly the composition of oil of amber (Völckel, Annalen, 88, 139). Nitric acid converts it into a resin, having the odour of musk and the taste of bitter almonds.

Boussingault obtained from the asphalt of Bechelbrunn a pale-yellow oil, *petrolene*, having a faint taste and bituminous odour, of sp.gr. 0·891 at 21°, and boiling at 280°.

By heating asphalt to 250° for 48 hours, the volatile oils are driven off; a black solid substance, *asphaltene*, is obtained. It becomes soft and elastic about 300°.

The purest asphalt is found on the shores of the Dead Sea and in the pitch lakes of Trinidad and Mexico. Rocks more or less impregnated with bitumen, to which the name earthy or crude asphalt is given, are found at the Poldice mines, Cornwall; near Matlock, Derbyshire; at Haughmond Hill, Shropshire; at the Hotwells, near Bristol; in the limestone near Glasgow; the freestone near Edinburgh; and generally throughout the Orkneys. Large deposits occur also at Seyssel, Dépt. de l'Ain; at Bechelbrunn and Lobsann, Lower Rhine; at Bastennes and Dax, in the Dépt. des Landes; in the Val de Travers, Neuchatel and other places.

Asphalt is separated from the minerals with which it is associated either by melting the mass, allowing the earthy matters to subside and removing the bitumen; or by boiling with water, which causes the bitumen to run out in the melted state; or by the action of hydrochloric acid, which dissolves the calcium carbonate and leaves the asphalt; or with oil of turpentine, which dissolves out the bitumen. Murrie (J. Soc. Chem. Ind. 3, 182) describes the

methods used in Italy for the extraction of bitumen from crude asphalt.

The Val de Travers asphalt contains about 20 p.c. of bitumen, and it only requires the addition of 6 to 8 p.c. of mineral or coal tar to convert it into a plastic, workable mastic of good quality for pavements and hydraulic works.

The modern method of laying down asphalt pavement is to first prepare a foundation of concrete the surface of which is carefully flattened. On this even surface, when thoroughly dry, the melted asphalt is spread with a wooden trowel, and the surface is finally smoothed over. The liquid Val de Travers, Limmer's, and Barnett's asphalts used for this purpose are all mixed with grit or sand, and so present rougher surfaces than those pavings which consist of asphalt alone. Brande (D. R. P. 4993, 1878) mixes ground slag with the asphalt instead of sand.

Another method of paving is to break up the bituminous ore, and heat the fragments till they crumble to powder. A layer of this hot powder, from 16 to 20 inches thick, is laid on the dry concrete and compressed by stamping with hot irons.

Artificial asphalt, or gas-tar asphalt, is a mixture of chalk, sand, or limestone with the thick, pitchy residue obtained by evaporating the more volatile portions of gas tar. The mineral substance must be heated to expel moisture and adhering air, and then added to the strongly heated pitch.

In addition to the use of asphalt for pavements, water-tight tanks, and coatings for iron tubes used for conveying gas or water, &c., it is used in photography, in photo-lithography, and photo-engraving, owing to the asphalt becoming insoluble in turpentine after exposure to light. In the latter case copper plates are covered with a thin coating of pure asphaltum, or bitumen of Judæa, dissolved in benzene or chloroform. When dry, the plate is exposed behind a film to bright sunlight for half an hour, and then developed by first softening the soluble portion of the asphaltum with olive oil, to which subsequently a little turpentine is added. As soon as the lines are bare the turpentine and oil must be washed away by the action of water.

Methods for preparing asphalt for paving and other purposes are described by Dagusan (D. R. P. 4999, 1878; Dingl. poly. J. 232, 547); Kalilbetzer (D. R. P. 5646, 1878); Zadig and Neuberg (D. R. P. 5678, 1878; Dingl. poly. J. 233, 490); Clark (Eng. Pat. 8036, 1884; J. Soc. Chem. Ind. 5, 183); Kettmann (Eng. Pat. 12425, 1884; J. Soc. Chem. Ind. 4, 675); Richter (Siefenseid Zeit. 23, 272; J. Soc. Chem. Ind. 2, 474).

Native asphalt can be distinguished from artificial asphalt by extracting with carbon disulphide, filtering, evaporating to dryness, and heating the residue till it can be ground to a fine powder; 0·1 gram is treated with 5 c.c. of fuming sulphuric acid for 24 hours, and is then mixed, with continuous stirring, with 10 c.c. of water. If pitch or coal tar be present, the solution will be of a dark-brown or blackish tint; if not, the solution will be of a light-yellow colour (*v.* PITCH).

ASPHODEL. The tuberous roots of *Asphodèle de Sardaigne*, of *Asphodelus ramosus* (Linn.), and other species of the same genus, contain a fermentable substance from which alcohol may be prepared (*cf.* Rivière and Bailhache, Compt. rend. 1895, 121, 659). By drying and coarsely grinding the tubers, Landerer obtained a powder which, mixed with water, formed a strong glue. Badoil and Lienders obtain tannin from the pulp left after the extraction of the alcohol.

ASPIDIN *v.* FILIX-MAS.

ASPIDOSAMINE and **ASPIDOSPERMINE** *v.* VEGETO-ALKALOIDS.

ASPIRATORS. Aspirators are used to draw air or other gases through any apparatus connected with them, and were probably first employed by Brunner in his analyses of air, 1830–1840 (Pogg. Ann. 20, 274; 24, 569; 31, 1). The process of aspiration or inhaling of air is, however, most common, being necessary to the life of animals and to the ventilation of buildings, mines, &c., to change the air so that it may support life. In other analyses of air by Dumas and Boussingault, an exhausted globe or jar was used as an aspirator (1841, Ann. Chim. Phys. [3] iii. 257). When a vessel is emptied of liquid, air must enter to take its place, and the common aspirator, in its various forms, is a vessel with two openings, the lower to serve as outlet for the water or liquid, and the upper as inlet for the air or gas to be aspirated. With suitable fittings a siphon may be used instead of the lower opening, or the apparatus may be modified into a bell-jar standing over a basin or large jar, the air being drawn in through the neck of the bell-jar. This is Mohr's aspirator, which is sometimes poised like a gasholder to facilitate filling and emptying of the bell-jar (Mohr, Lehrbuch der Titrirmethode, 1855, Brunswick).

From their introduction, aspirators were used not only to draw in gases through apparatus and reagents employed, at a regulated rate, but also to measure the gases so manipulated by simply measuring or weighing the liquid run out of the aspirator. For approximate readings aspirators of glass may be graduated, and those of metal may be provided with gauge glasses.

Numerous forms of the simple aspirator have been invented by Brunner, Regnault, Mohr, and others. Fig. 1 is perhaps the form in most frequent use, and is generally of glass, plain or graduated. Fig. 2 is a very convenient form, described by Clemens Winkler (Industrie-Gase, 1877, 39–41) constructed of zinc plate and supported on a wooden tripod. The second tap below, on the side tube, is useful in filling the aspirator with water. Fig. 3 is the form often used in testing the gases from chemical works. It is simply a cubical or rectangular box made

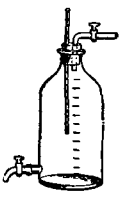


FIG. 1.

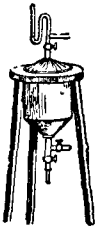


FIG. 2.

of sheet lead, with a graduated gauge glass, and can be opened at A to fill it with water.

Double aspirators. In short operations the simple aspirator requires no refilling nor special attention after the taps are adjusted. To obviate the inconvenience of stopping to change or refill that would be necessary in longer operations, Brunner, Boisgiraud, Dancer, Muencke, and others have contrived double aspirators so connected that each vessel is alternately above and below, and one or other always ready for use. The aspirating bottles may be mounted on a common axis as in Dancer's swivel aspirator

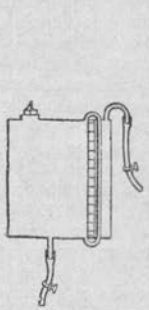


FIG. 3.

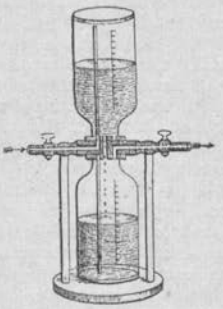


FIG. 4.

Fig. 4 (Chem. News, 1864, 10, 295). These swivel aspirators are very convenient, but the difference of water-level in the two bottles is not under the control of the operator and varies between the height of one bottle and a very small minimum.

Figs. 5 and 6 show an arrangement devised

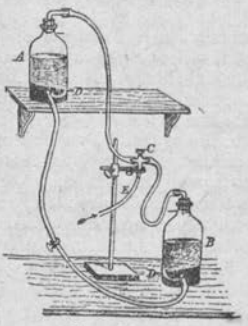


FIG. 5.

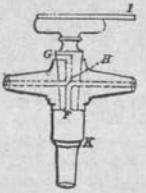


FIG. 6.

by the author, which has certain advantages. The bottles A and B are connected as shown, being raised and lowered alternately. The four-way tap C (shown larger in Fig. 6) has its index I turned towards the upper bottle in aspirating and towards the lower bottle in blowing. It is made from a good gas tap by boring up the centre of the plug at F, leading out the hole at G. A small piece of metal H is then fitted and soldered diagonally where the holes cross, a piece of tubing K soldered on to the socket of the tap, and an index I above the plug.

Paraffin wax is used to adjust the bottles for exact measurement, and to obtain a fine adjustment below at D, as well as above, by a mark on the neck of the bottle. The proper quantity of melted wax is run through a wide tube into the warm bottle slightly tilted. A passage from the tubulure to D at the side of the bottle is secured by pushing an indiarubber tube through the tubulure and fixing it in the proper position before the wax is run in, and after the wax is quite solid this tube is drawn out. The passage should be curved, so that on emptying the bottle of water the water runs out to the mark at D. The bottles are then adjusted by weighing their content of water between the marks and adding or removing paraffin till at the standard temperature and pressure they hold the exact quantity of water corresponding to the volume required. In successive weighings of bottles so adjusted the differences should not exceed 0·1 gram. To avoid loosening of the wax from direct contact with the glass, the bottles should be preserved from changes of temperature and from mechanical vibration, &c.

Constant or automatic aspirators. Instruments of this class have been invented by Guthrie (Phil. Mag. [4] 15, 64) and by Bonny (Winkler's Technical Gas Analysis, trans. by Lunge, 17). In each of them a pipe from the water supply leads a constant stream of water into a vessel, which, when full, is emptied by a siphon, whose tube is of larger size than the supply pipe. The arrangement thus acts on the principle of the intermittent siphon, and the vessel is filled and emptied at regular intervals. In Bonny's instrument these are registered by a simple mechanism, and the total volume passed is known on measuring the volume passed in one operation.

The Sprengel and injector pumps may be used as constant aspirators (*v.* FILTER PUMPS). By means of a collecting box attached below the pumps to allow the gas and water to escape at different levels, the gas may be measured by passing it through a small gas meter (Davis, J. Soc. Chem. Ind. 211).

J. Grossman (Winkler's Industrie-Gase, 218) has invented a small mercurial aspirator, on the principle of the Geissler pump, with two reservoirs, which are alternately raised and lowered. It is fitted with registering apparatus.

In testing air and gases from confined places, works, &c., Angus Smith, Davis, and others have used small pear-shaped aspirators of indiarubber. These are emptied by simply squeezing in the hand. The air escapes by a valve, of which the simplest is a small slit in the rubber connecting tube, opening outwards like a Bunsen's valve. The rubber recovering its form draws a certain volume of gas through the testing apparatus, and it is easy to ascertain approximately the total volume of gas corresponding to any given number of times the aspirator has been filled. Another larger aspirator of this class is of bellows form, like a concertina, the folding part being of indiarubber. This aspirator is frequently used for filling by displacement jars or bottles with gas to be tested. The common single-barrel air pump or apparatus, on the same principle, is also applied in this manner as an aspirator.

At the British Association Belfast meeting, 1874, the late Prof. Andrews showed how an ordinary wet gas meter could be converted into an aspirator by applying motive power to the hollow axis of the drum, thereby causing it to suck in air at the inlet side and at the same time to measure the air on the meter index. Using

mercury as liquid in a cast-iron meter, a similar arrangement forms the basis of the Barr and Stroud air pump applied in the evacuation of bulbs for electric lighting lamps (J. Soc. Chem. Ind. 1896, 640; Eng. Pat. 13188, July, 1895).

T. F.

ASPIRIN. Trade name for acetyl salicylic acid $C_6H_4(COOH)O{\cdot}CO{\cdot}CH_3$, used as an anti-rheumatic.

ASSAYING. Assaying, 'the trial of metals,' a term originally applied only to the testing of gold and silver, is now usually extended to the determination of the quantity of the valuable metal in an ore or metallurgical product. It is also sometimes taken to include the estimation of any element which may prejudicially affect the value of the ore, but it is more usual to discuss this together with such work as the complete analysis of ores, slags, furnace materials, fuel, &c., under the heading of 'metallurgical analysis.' A brief account of some of these sections is given below.

The art of assaying is of great antiquity. The use of the touchstone for testing gold in India was referred to by Mathuranatha (Hist. of Hindu Chemistry, by Ray, ii. 231), and was probably known in the Greek world at least as early as B.C. 700, when the first electrum or gold-silver coins were manufactured. At any rate the touchstone found its way into Greek mythology. The testing of gold alloys by cementation was described by Pliny, by Strabo, and in the eighth century A.D. by the Arabian Geber, who was also familiar with the method of cupellation, and is reputed to have discovered nitric acid. The parting assay of gold with the aid of this acid is referred to in a decree of Philippe de Valois in the year 1343, confirming its use in the French Mint. Alloys of silver with copper were tested by observing the degree of blackening caused by heat in the Roman Mint under the Republic (Rochon, Essais sur les Monnoies, 17, 1792).

It is probable that ores were not valued except by inspection until the Middle Ages. The first clear references to ore-assaying are to be found in the writings of Biringuccio, Agricola, and Ercker in the sixteenth century, but the art was evidently regarded by these authors as already ancient at the time at which they wrote. Ercker, writing at Frankfort in 1580, describes the fire-assays not only of several different kinds of gold and silver ores, but also of the ores of copper, lead, tin, antimony, iron, mercury, and bismuth. Assaying by means of 'wet methods,' volumetric, gravimetric, and electrolytic, is of comparatively recent introduction (excepting the parting assay of gold), but has now in great part superseded the ancient processes involving the use of furnaces.

Sampling.—Whether the material to be assayed is a portion of a vein underground, a heap of broken ore, pigs of metal, or a delicate piece of jewellery, in every case a representative sample must be obtained. In the case of ore *in situ* underground, pieces are taken from a number of different points and either mixed or examined separately. Ore which can be moved is reduced in bulk either by hand or by machinery, and is generally crushed finer between each successive reduction in bulk. Every second, fifth, tenth, or twentieth shovelful or car-load may be set aside as a sample, or the whole heap may be made into a perfect cone, which is flattened and divided into four quarters along two diameters. Two opposite quarters are removed and mixed, and the process of 'coning and quartering' repeated as often as necessary. A heap or vat of ore or tailings, which must be sampled without being moved, is pierced at regularly spaced intervals by a sampling tube which resembles a cheese-taster, and withdraws a cylindrical sample extending to the bottom of the vat or heap.

In automatic sampling machines, which are much used in Western America, the crushed ore is made to slide down an inclined plane or rotating cone, and a portion of the stream of ore is deflected and set aside as a sample. Those machines are preferred which momentarily take the whole stream of ore at regular intervals of time. Further reduction in the laboratory is effected by coning and quartering or by a machine such as the *riffle* or *sampling tin*, which consists of a series of metal troughs arranged side by side and fastened at equal distances from each other. A stream of ore let fall on it is in part retained by the troughs and in part passes through.

The final grinding of the ore is effected by means of an iron pestle and mortar, or of a large hammer with a curved face sliding on an iron plate (or *buckboard*), or by some form of rolling or grinding mill. The crushed ore is passed through a sieve, the fineness of which varies according to the ore and the method of assay. If a panning test is required, a 20-mesh sieve (*i.e.* one with 20 holes to the linear inch) suffices. For most fusions, *e.g.* dry lead assay, a 60-mesh sieve is used. Gold ores are crushed through an 80- or 100-mesh sieve, and in the case of telluride ores of gold, the best results are obtained by using 120-mesh sieves. Before it can be passed through a fine sieve, the ore must be dried, so that the *moisture* is determined on coarsely crushed ore by drying at 100° on a water-bath, or, if the dry material is not likely to be affected in any way by a somewhat higher temperature, it is heated on a sand-bath. In crushing rich gold and silver ores, mint sweepings, &c., pieces of metal are found which become flattened out and are caught on the sieve. These 'metallics' are treated separately, and the value calculated on the weight of ore from which they were derived.

The dried and crushed sample is thoroughly mixed by means of a spatula in a basin, or on rubber-cloth, before the portion required for assay is weighed out. If stored in a bottle or tin, the movement of the vessel causes the heavy particles to settle, so that the material at the bottom becomes richer than that at the top.

Ingots of metal are sampled by cuts taken from the corners or edges, as in the case of refined gold and silver, or by drillings from a number of different spots, as is sometimes done in the case of iron and steel. Pigs of argentiferous lead are sometimes sampled by drillings or saw cuts. Base gold and silver ingots, and in many cases ingots of steel and pigs of lead, are melted and stirred, and a portion dipped out and granulated by pouring into water, or cast into a little ingot. Coins are sampled in various ways, silver coins being seldom uniform

in composition. The simplest method applicable to all is to roll them out and cut them into a large number of little pieces, so that all parts of the coin may be represented in the portion taken for assay. This method is adopted in the Philadelphia Mint, but is not in general use, other more complicated methods being preferred. Gold and silver wares are usually pickled, and are richer on the surface than in the interior. In sampling them, it is accordingly necessary to remove the outside by scraping and then to scrape off a portion of metal for assay.

The *preliminary examination* of ores includes careful inspection, which is all the more useful if some comparatively large pieces are included in the sample. The proximate constituents, such as quartz, pyrites, magnetite, galena, &c., are thus observed, and the proportions in which they are present roughly estimated, this information being required in making-up furnace charges. Frequently a concentration test is made in a miner's pan (a flat-bottomed sheet-iron pan about 20 inches in diameter, and 3 or 4 inches deep, with sloping sides) or a vanning shovel, or in any basin, pan, or even clock-glass available. For this purpose a portion of 25 grams or more is weighed out, stirred and shaken with water by a circular motion on the shovel, and the lighter particles rinsed away and caught in a basin. Finally by a combination of the circular motion, and a series of jerks, the denser particles are thrown up and the lighter ones washed down the shovel. The concentrates are examined with a lens or separated, dried, and weighed, or treated with acid, or examined by means of the blowpipe, or in other ways, in order to determine the presence or absence of elements likely to interfere with the method of assay chosen. The vanning shovel is used particularly with tin ores, but may be applied to any others. Panning tests are especially useful in the examination of gold ores, but are also required to determine the nature of the 'mineral' or compounds of the heavy metals in almost all ores. The test may be applied to half a gram of ore in a watch-glass, if no more can be spared.

The furnaces used by assayers are the muffle furnace, and the melting or wind-furnace.

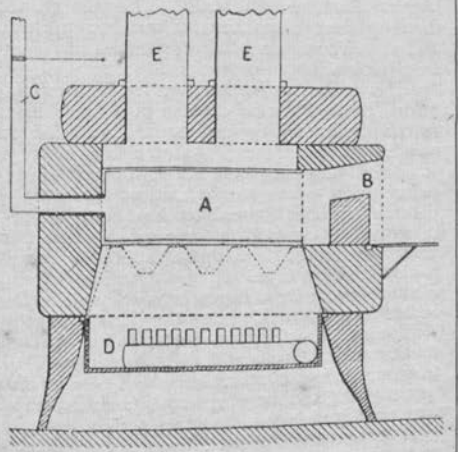


FIG 1.

The *muffle furnace* consists of a small oven or muffle of refractory fireclay open at the front, and having an arched top. It is heated by coal, coke, oil, gas, or electricity. Muffles vary in size according to the amount of work to be done, but those used at the Royal Mint may be considered full size. Sectional views of one of these furnaces are shown in Figs. 1 and 2. The muffle A is 14½ inches long, 8¼ inches wide, and 5 inches high, inside measurements, with walls about ⅝ inch thick. The mouth is closed by the firebrick B and by a sliding plate. Air enters through holes in the sliding plate and passes out at the back through the tube C,

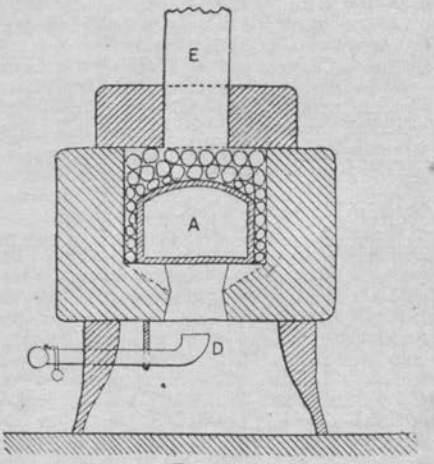


FIG. 2.

which has a sliding damper and leads into the main flue. The fuel is ordinary gas, supplied by a row of bunsen burners D, and complete combustion of the gas may be aided by clay fireballs surrounding the muffle. The flues E E carry off the waste gases. The furnace walls consist of firebrick bound with iron and covered with a thick layer of magnesia and asbestos to check radiation. No chimney stack or forced draught is required for this furnace.

A *melting furnace* adapted for the use of coke as fuel and suitable to make fusions in assay operations, is shown in section in Fig. 3, in which A is the fireplace, B the flue, C the ashpit, D the damper, and E the firedoor. The most useful size of the fireplace is about 9 inches square, and about 10 inches in depth from the firebars to the flue. The furnace is built of brick and lined with firebrick. It is bound with angle iron or covered with iron plates bolted together and furnished with tie rods. Gas-melting furnaces with natural draught

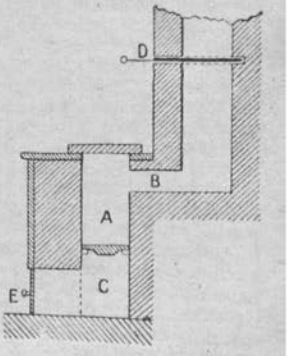


FIG. 3.

or using a blast of air are less common. The fluxing crucibles (*a*, Fig. 4) consist of fireclay or a mixture of plumbago and fireclay, or, in the assay of galena, of wrought iron. They are of different sizes and shapes, the best-known being the Battersea (round, Cornish, and triangle), French, Hessian, and Colorado cru-

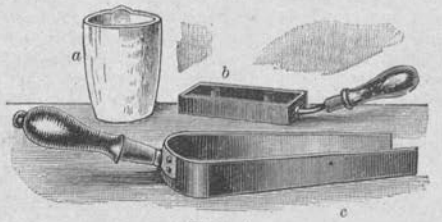


Fig. 4.

cibles, the last-named being used for making fusions in the muffle, a common practice in America. Most crucibles require careful annealing before being used. Roasting dishes made of fireclay (*a*, Fig. 5) are for the roasting of ores; scorifiers (*c*) are used in the process of scorifica-

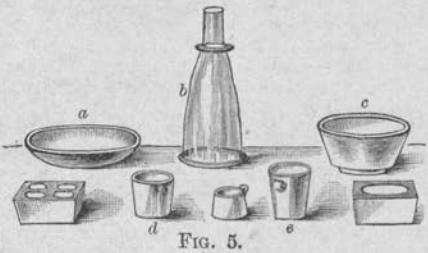


Fig. 5.

tion; cupels of various shapes and sizes (*d*, *e*) are made of compressed bone-ash or magnesia, and are required in the assay of the precious metals. The bone-ash cupels may be made by the assayer, and must be carefully dried before use. Magnesia cupels are usually bought ready-made. A parting flask is shown in

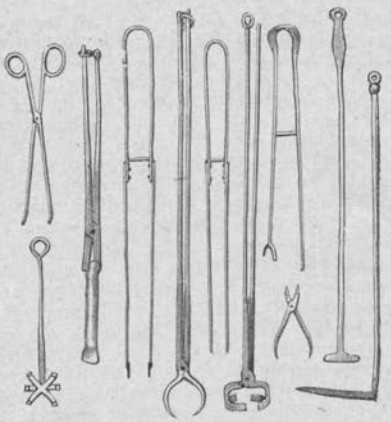


Fig. 6.

b, Fig. 5. The furnace implements (Fig. 6) consist of basket or circular tongs for lifting crucibles out of the furnace, pouring tongs, cupel tongs, scorifier tongs, and button tongs, with various scrapers, pokers, &c. Iron slag-moulds (*b*, Fig. 4) are required for casting the results of scorifications and of fusion assays, and hammers, anvils, slag hoops, and other implements are also required. The charging scoop (*c*, Fig. 4) is required for charging metal, &c., into red-hot crucibles.

The *reagents* used in fire assay may be classed as fluxes, agents for reducing, oxidising, sulphurising, and desulphurising, and covers to protect the contents of the crucible from the action of the air, furnace gases, &c. Generally speaking, an ore consists of compounds of a heavy metal or metals (the mineral), together with a quantity of earthy materials, such as quartz, silicates, &c. (the gangue). It is required to reduce the valuable constituent to metallic form, and to incorporate the remainder of the ore in a fusible slag, through which the particles of metal may settle to the bottom, where they collect in the form of a button. Sometimes a regulus or matte (sulphide of a heavy metal) or a speise (arsenide of a heavy metal) forms a separate layer between the metal and the slag, and a cover, say, of common salt, may be provided which is lighter than silicate slags and floats on the top. On breaking open a cold crucible in which a fusion has been made, there are, therefore, frequently four layers.

The principal fluxes used are sodium carbonate, which forms fusible mixtures with acid (siliceous) ores, and also acts as a desulphuriser, converting pyrites into a mixture of sulphides of iron and sodium which does not form a regulus, but is dispersed through the slag. Carbonate of soda is generally used in the form of powdered bicarbonate, which gives up half its carbonic acid without fusion. Soda crystals give up their water of crystallisation with ebullition, and are not suitable unless previously dried. Basic ores require borax, which forms fusible mixtures with oxides of iron, lime, &c.; and increases the fluidity of most charges. Crystallised borax powder on heating swells up enormously, gives up its water and fuses into a glass. The swelling may occasion loss in the assay if the crucible is too full. To avoid this, borax glass may be used, which is equivalent to about double its weight of ordinary borax. Litharge is a useful flux, especially for oxides of iron, copper, &c., but attacks and corrodes the crucibles. Fluor-spar is sometimes used, especially for phosphates. Sand is often required to protect the crucible from attack by basic ores.

The reducing agents are carbon (charcoal powder or lampblack), flour, tartar or argol (crude hydrogen potassium tartrate), and occasionally potassium cyanide. One part of charcoal is about equal to two parts of flour or five of tartar, but tartar also acts as a flux, being converted by heat into carbon and potassium carbonate. Black flux is a reducing mixture made by deflagrating one part of nitre with two and a half parts of argol.

The chief oxidising agents, which are also desulphurisers, are hot air, litharge or red lead, and nitre. Iron is often used as a desulphurising agent. The ordinary materials used as covers are borax and common salt.

The *balances and weights* do not differ, as a rule, from those used in ordinary chemical

analysis, the most notable exception being in the case of those used in the assay of gold and silver. The proportion of these metals present in ores is reported in troy ounces, pennyweights, and grains per ton, or sometimes in ounces and decimals or in pennyweights and decimals. The weight of ore taken for assay accordingly contains as many milligrams as there are ounces troy in a ton (29,166 in a ton of 2000 lbs., and 32,666 in a ton of 2240 lbs.). This weight of 29·166 grams is called an *assay-ton* (or A.T.), and boxes of weights made up of assay-tons and decimals are used by many assayers. Then the gold extracted from the sample of ore is weighed in milligrams, and can be reported without calculation. In the assay of gold bullion the weights commonly range from '1000' downwards, where 1000=0·5 gram or some other unit such as 5 grains. Much tedious calculation is avoided by thus marking the weights so that their face-value gives at once the result of the assay. Again, in assaying silver by precipitation as chloride (India Mint method, see p. 327), since 18·815 grains of pure silver are contained in 25 grains of chloride, it follows that if 18·815 grains of an alloy be always taken for assay, and the resulting chloride be weighed out with a series of weights the largest of which is marked 1000, and is equal to 25 grains, and the others are marked correspondingly, then the subsidiary weights of this series will indicate the result of the assay without calculation. A similar series can, of course, be arranged for any special purpose.

The balances used for weighing gold and silver in bullion assays are light and delicate, taking about 2 grams as their maximum of weight, and turning to one hundredth of a milligram. Usually, one division of the ivory scale is made equal to 0·05 mg. Balances for weighing the parted gold in ore assays are still more delicate. The maximum weight which they can carry is only 1 gram or even less, and they turn with one-hundredth or in some cases only one five-hundredth of a milligram. Milligram and half-milligram riders are used, but the final reading is always based on the deflection from the zero position of the pointer, measured by the number of divisions on the ivory scale covered by the swing. At the present day short beams of 6 inches, 4 inches, and even 8 cm. in length, are in use, so that the balances are very rapid in action in spite of their sensitiveness.

In quantitative blowpipe work on gold and silver, it has been found possible to dispense altogether with a delicate balance, and to use an ivory scale (Plattner's scale), by which the diameter of the bead of metal is accurately measured. The principle has been extended in the assay of poor materials, and beads of microscopic dimensions are placed on the stage of a microscope and measured by means of a micrometer eyepiece. In this way L. Wagoner (Trans. Am. Inst. Mining Eng. xxxi. 1901, 798) obtained a close approximation to the weight of beads of silver of 0·02 mm. in diameter, which weighed about 0·00004 mg.

The above summary has special reference to the requirements of a laboratory for making dry or fire assays. For wet assays, the apparatus and reagents are those of the ordinary analytical laboratory (*v.* ANALYSIS).

In all methods of assaying, wet or dry, time must be considered as well as accuracy. It is sometimes important to arrive at a result in the course of an hour or less, and some of the methods described are intended for such emergencies, when extreme accuracy must be sacrificed. It is also necessary to observe that assay methods are intended to be comparative, and wherever it is possible check assays on similar materials of known composition should be made side by side with the assays of ores or other bodies requiring examination, and a correction applied to the results. In the following pages, only methods in common use in assay offices are described. The methods of ordinary analysis are generally omitted or made the subject of brief reference.

Aluminium. There are no special methods of assaying the ores of this metal. The silicates are broken up, and the silica removed as usual (see p. 329), and the acid solution of the bases is treated so as to separate the metals contained in it. Aluminium is precipitated and weighed as phosphate $AlPO_4$, or oxide Al_2O_3. It is sometimes weighed as oxide together with oxide of iron Fe_2O_3, and also P_2O_5, if these constituents are present in the ore. The last mentioned constituent is of course combined as phosphate. The phosphorus and iron are then determined, aluminium being estimated by difference (Low's Technical Methods of Ore Analysis, 1st ed. 22).

Antimony. The antimony in ores may be determined by fusion with cyanide of potassium or with iron (avoiding excess) and black flux, but the results are unsatisfactory. The sulphide of antimony in an ore may also be approximately determined by charging 500 grams of ore broken to nut-size into a clay crucible with a perforated bottom. This crucible is fitted into another of about the same size, and the joint carefully luted. A cover is also luted on, and the whole is slowly raised to a red heat. The sulphide of antimony fuses and liquates into the lower crucible, from which it can be detached when cold, and weighed. The fused sulphide of antimony, if pure, contains 71·7 p.c. of the metal. The valuation of antimony sulphide ores is usually effected, according to Bedford McNeill (Berenger's Assaying, 11th ed. 226), by having recourse to the ordinary smelting operation, which is to be used in treating the ore on the large scale. Charges of about 20 kilos. of ore are used for the valuation.

The wet methods of estimation of antimony in ore are far more accurate than those referred to above. The ore is fused with sulphur and sodium carbonate, and then digested with water. A solution of an alkaline sulphocompound of antimony is thus obtained, from which a mixture of antimony and arsenic sulphides and free sulphur is precipitated by the addition of dilute hydrochloric acid. After the arsenic has been separated, the antimony sulphide is weighed or is oxidised by fuming nitric acid, and weighed as Sb_2O_4. Ores may also be attacked by hydrochloric acid. The antimony in the separated sulphide may be estimated volumetrically, dissolving the sulphides in hydrochloric acid and chlorate of potash, warming to expel the chlorine, adding an excess of potassium iodide, and titrating

with thiosulphate of soda (J. Soc. Chem. Ind. xv. 255).

Arsenic. The determination of arsenic in ores and metallurgical products is usually made by Pearce's method, which consists in fusing about 0·5 gram of the ore with 5 grams of a mixture of equal parts of sodium carbonate and nitre, dissolving out the soluble arsenates of the alkalis and precipitating the arsenic in a neutral solution by means of silver nitrate. The precipitated brick-red silver arsenate Ag_3AsO_4 is filtered off, dissolved in nitric acid, and the silver in it determined by Volhard's thiocyanate method. The amount of arsenic present can then be calculated (Low's Ore Analysis, 41). Small quantities of arsenic in metals and minerals may be separated by distillation with ferric chloride and calcium chloride in a hydrochloric acid solution, the distilled arsenious chloride being condensed in a vessel of cold water (Berenger's Assaying, 384). (For arsenic in steel, *see* p. 325.)

Bismuth, if present in an ore in the metallic state, may be determined by liquation, the method of procedure being similar to that used in liquating sulphide of antimony (*q.v.*). The bismuth in an ore may also be determined by fusing it with fusion mixture, common salt, and cyanide of potassium. These methods are inexact, and bismuth is usually determined by being weighed as Bi_2O_3 after precipitation as carbonate, or as BiOCl on a weighed filter or a Gooch crucible after being dried at 100°. Bismuth in metallic lead is precipitated and weighed as BiOCl, and in metallic copper it is detected by the colour given to lead iodide. (For estimation of bismuth in copper, *see* p. 322.)

Chromium occurs in chrome-iron ore and sometimes in other iron ores, in pig-iron and in steel. Small quantities of chromium in iron ores, after separation from other metals and earths, are precipitated by lead acetate in an acetic acid solution, and weighed as $PbCrO_4$, or, in the alternative, reduced by sulphurous acid and the chromium precipitated from the green solution by means of ammonia and weighed as Cr_2O_3. Chrome-iron ore is assayed by a volumetric method based on the oxidation of ferrous iron by chromium in the form of chromate. The chromium is oxidised by peroxide of sodium (J. Iron and Steel Inst. xlviii. 153). The ferrous iron is added in the form of a weighed amount of ferrous ammonium sulphate or of a weighed amount of metallic iron dissolved in sulphuric acid. The excess of ferrous iron present in the solution containing the chromium is titrated with permanganate. Chromium in steel is precipitated and weighed as chromium phosphate (Chem. News, lvii. 1888, 153), or as chromic oxide Cr_2O_3.

Cobalt. (*See* **Nickel**, p. 326.)

Copper. The principal ores of copper are (*a*) native copper; (*b*) sulphide ores, copper pyrites or yellow ore, erubescite or purple ore, grey copper ore, &c.; (*c*) oxidised ores, malachite, silicate of copper, &c. The treatment of copper ores results in the production of copper matte or regulus containing from 30 to 50 p.c. of copper, and cement copper or copper precipitate, containing 70 p.c. or more of metallic copper. In addition to these materials, ordinary commercial standard copper, refined copper, and the alloys of copper require to be assayed.

The chief methods in use are as follows:—

(1) *Dry or Cornish assay*, long used in connection with the sale of copper ores, but applicable chiefly to mattes and rich sulphide ores. It is especially unsatisfactory when dealing with poor ores, but gives low results in all cases, the loss, according to Beringer, ranging from 2 p.c. of the copper present in the richest materials to 33 p.c. of the copper in 2 p.c. ore. It consists in fusing the calcined regulus for metallic copper and refining the copper. Rich oxidised ores are fused for metal at once. The amount of ore taken for assay is 400 grains, but with rich material only 200 grains or even 100 grains are taken. The fluxes vary with the nature of the ore, in which there may be too much sulphur and iron, as in copper pyrites, &c., or too little, as in grey copper. The following are examples of the charges:—

	A. Copper pyrites	B. Grey copper ore
Ore	200 grains	100 grains
Nitre	50 ,,	—
Lime	200 ,,	200 ,,
Fluorspar	200 ,,	200 ,,
Glass	150 ,,	150 ,,
Borax	150 ,,	150 ,,
Hæmatite	—	15–20 ,,
Sulphur	—	25–30 ,,
Argol	—	30 ,,

The charge is fused in a 'large copper' crucible at a low red heat, which is gradually raised. After about 15 minutes the charge is poured into a conical mould, and, as soon as the slag is solid, it is taken up by tongs, dipped into water, and allowed to dry. When treated in this way, the slag breaks up readily. The regulus is detached by a hammer and crushed to powder in an iron mortar. It should be reddish-brown in colour and contain about 50 p.c. of copper and 20 p.c. of iron. It is roasted in a Cornish crucible in the melting furnace or in a roasting dish in the muffle, at a low but increasing temperature, with continuous stirring at first. When 'sweet,' *i.e.* not smelling of sulphur, at a full red heat, it is mixed with a little charcoal powder, and re-roasted to decompose sulphates. It is then crushed again, if necessary, and fused in the same crucible with argol, borax, and sodium carbonate. A high temperature is required, and the charge is poured in about 15 minutes. The slag is detached and cleaned by a second fusion with more argol and sodium carbonate. The 'coarse copper' obtained in this way is refined by being charged into a very hot crucible and melted. The impurities are oxidised by the air and form a ring of oxides round an eye of copper. Then refining flux, which consists of a deflagrated mixture of nitre, argol, and common salt, is added, and 2 minutes later the copper is poured, and if it is found to be at 'tough pitch,' it is weighed. The slag contains copper, and must be cleaned. (For full details of the method, *see* Percy's Metallurgy, i. 1861, 454–478.)

(2) *Electrolytic assay of copper.* The weight of ore taken for assay depends on its richness, a convenient amount of metallic copper for electro-deposition being from 0·1 to 0·5 gram. When using this method or any of the other

wet methods, the copper must first be brought into solution and usually separated from other metals. Oxidised ores may require merely to be treated with hydrochloric acid. Sulphide ores, mattes, copper precipitate, &c., are attacked by nitric acid, evaporated to dryness, and taken up by hydrochloric acid. Copper slags are fused with sodium and potassium carbonate (fusion mixture), and a little nitre, and are then digested with water and hydrochloric acid. The copper is precipitated from its hydrochloric acid solution by means of sulphuretted hydrogen or (after evaporation with sulphuric acid) by sodium thiosulphate, and the sulphides are filtered off and redissolved in nitric acid. For the electrolytic assay, the solution obtained in this way is diluted, warmed, and filtered into a 200 c.c. flask, and made up to about 100 c.c., of which from 2·5 to 5 p.c. should be nitric acid. Platinum electrodes (spiral and weighed cone or cylinder) are then placed in position, and a current from two Daniell cells in series is passed through for 16 or 17 hours. The cylinder is removed from the colourless solution, washed with water and afterwards with alcohol, dried in a water-oven, and weighed. The copper precipitate should be salmon-red in colour. The solution still contains a little copper, which is estimated colorimetrically, ammonia being added, and the colour, after filtration, compared with those of standard solutions containing known amounts of copper. Silver, mercury, bismuth, arsenic, and antimony interfere with the process, being deposited with the copper. Mercury, however, is separated on dissolving the sulphides in nitric acid. Bismuth turns the copper dark grey, but is not deposited until most of the copper has been thrown down. Arsenic and antimony darken the copper deposit, but may be driven off by heating to dull redness. Lead makes its appearance at the anode. The electrolytic assay is suitable for all materials containing copper (*cf.* ELECTROLYTIC ANALYSIS).

By rapidly rotating the cathode a coherent deposit can be obtained even when a strong current of 10 to 12 amperes per 100 sq. cms. of cathodic area instead of the usual current of 0·5 to 1·0 ampere is used. The time required for the deposition of the copper may thus be shortened to a few minutes (Amer. J. Sci. 1903, xvii. 320, xviii. 56; J. Amer. Chem. Soc. xxv. 896; Chem. Soc. Trans. xci. 373).

(3) *The volumetric assay of copper.* There are two main processes—the potassium cyanide and the iodide methods. Both are in wide use in the assay of ores, alloys, &c. In preparing to use these methods, the copper is brought into solution, and may be separated from other metals, &c., as already described, with any further precautions necessary to remove special impurities. With ordinary pyritic ores, however, containing no zinc, silver, nickel, or cobalt, it is sufficient, in preparing for the cyanide process, to heat the ore gently with concentrated nitric acid to which a little sulphuric acid has been added. It is then diluted, an excess of ammonia or of Na_2CO_3 added, the bulk made up to some convenient amount such as 300 c.c., and the solution titrated with potassium cyanide. The blue solution is decolourised, and when overdone changes to a straw-yellow colour. The results are affected by time, temperature, degree of dilution, and by the amounts of ammonia and of ammonium salts. The conditions of the check assays on pure copper and those on ores, &c., must therefore be identical, and ferric hydrate, for example, must be present either in both or in neither. The standard cyanide solution, which decomposes somewhat rapidly, contains about 42 grams KCy to the litre, and 100 c.c. of this is equivalent to 1 gram of copper. The reaction, according to Beringer, is represented by the equation:

$$CuSO_4+4KCy=2KCy.CuCy_2+K_2SO_4.$$

The quantity of copper usually present in an assay is about 0·5 gram. At the finish the effect of an addition of 0·5 c.c. of cyanide is readily observable. Zinc, silver, nickel, and cobalt interfere with the assay, and must be removed before titration.

In the iodide method, the alloy or the sulphide of copper separated from the ore is dissolved in nitric acid, evaporated almost to dryness in order to expel nitrous fumes, and diluted. The solution is then filtered if necessary, and carefully neutralised with sodium carbonate, avoiding excess. One c.c. of acetic acid is then added, which should be enough to redissolve the precipitated copper. Next, after cooling the flask, an amount of about 5 grams of potassium iodide crystals is added (or not less than ten times the weight of the copper present); the solution is diluted to a fixed amount, say 50 c.c.; and the liberated iodine is at once titrated with a solution containing 39·18 grams sodium thiosulphate (equivalent to 10 grams of copper) to the litre. The reactions are represented by the equations:

$$2CuSO_4+4KI=Cu_2I_2+2I+2K_2SO_4.$$
$$2Na_2S_2O_3+2I=2NaI+Na_2S_4O_6.$$

When the yellow colour is almost discharged, 2 c.c. of fresh starch solution is added, and the addition of the thiosulphate continued drop by drop until the blue colour disappears and does not return within 2 or 3 minutes. The effect of one drop or 0·05 c.c. of standard solution, equivalent to 0·5 mg. copper, is observable. The solution is standardised with pure electrolytic copper. Ferric acetate, arsenic, lead, and large quantities of sodium acetate may interfere with the titration. According to J. W. Westmoreland (Beringer's Assaying, 441), sodium acetate counteracts the interference of arsenic and bismuth, and the bad effect of large quantities of sodium acetate is removed by doubling the amount of potassium iodide added. Iron, if present, is precipitated by ammonium phosphate (J. Soc. Chem. Ind. v. 48). Instead of neutralising with sodium carbonate and acidifying with acetic acid, an addition of 20 c.c. of a saturated solution of zinc acetate may be made (A. H. Low).

The colorimetric method of assaying copper is sometimes used in the case of very poor ores, or generally whenever the quantity of copper present is small. Reference has been made to it above.

Examination of commercial copper. Electrolytic and Lake copper are generally nearly pure, but some of the metal sold contains as much as 2 or 3 p.c. of impurities. The most important of these are arsenic, nickel, oxygen, and

phosphorus; but antimony, bismuth, cobalt, gold, iron, selenium, silver, sulphur, and tellurium may also be present. The impurities to be looked for in copper which has passed a high conductivity test are mainly bismuth, selenium, and tellurium. Arsenic and phosphorus are separated as iron arsenate and phosphate mixed with acetate. Gold and antimony are separated by dissolving the copper in nitric acid, and silver is precipitated as chloride or bromide from a nitric acid solution. It may be collected in a precipitate of lead sulphate. Nickel is left in solution by precipitating copper electrolytically, or by sulphuretted hydrogen in an acid solution. Lead is detected by the blackening of the anode in the electrolytic assay, and is estimated as sulphate or chromate.

Oxygen is usually taken by difference, but is sometimes estimated by colorimetric determination of the quantity of the insoluble basic salt of copper formed by the reaction of silver nitrate with cuprous oxide (Hampe's method, Zeitsch. anal. Chem. xiii. 188). The equation representing the reaction is as follows:—

$$3Cu_2O+6AgNO_3+3H_2O = 2Cu_2H_3O_3NO_3+2Cu(NO_3)_2+6Ag.$$

The metallic copper is completely dissolved by the silver nitrate with separation of metallic silver. Bismuth is separated, according to Beringer, by precipitation by sodium bicarbonate. After redissolving in sulphuric acid, it is boiled with sulphurous acid and potassium iodide, and the bismuth in the yellow solution estimated colorimetrically. Tellurium and selenium (J. Amer. Chem. Soc. xvii. 280) are precipitated as iron tellurite and selenite by additions of iron nitrate and ammonia. The precipitate is redissolved in HCl, tartaric acid and potash added, and a current of sulphuretted hydrogen passed. The selenium and tellurium are subsequently precipitated by a current of sulphurous acid in a hydrochloric solution, and parted by boiling with potassium cyanide.

Gold. Gold is generally in the metallic state in its ores, either in the form of grains, scales, pellets, &c., in loose alluvial gravels, or in various forms embedded in quartz or other gangue in veins. It is frequently associated with iron pyrites, blende, &c., but the only native compounds are the tellurides. Besides these, the auriferous materials to be assayed comprise tailings or residues of ores after treatment, copper bottoms, pig lead, unrefined bullion, which contains silver, copper, and other metals, fine (*i.e.* refined) gold, and the commercial alloys used for coinage, plate, &c. The assay of gold ores and alloys is made with greater exactness than other assays, owing to the high value of the metal.

A *panning assay*, or concentration test is carried out as described on p. 317. The concentrates consist of 'black sand' or oxides of iron, titanium, &c., sulphides and arsenides, and sometimes grains of platinum. Free gold is sometimes visible, and is collected by grinding in a mortar with mercury, panning out the amalgam, and recovering the gold by distilling off the mercury or dissolving it in nitric acid. In either case the gold must be parted from the silver as described on p. 323. The panning assay of alluvial gold deposits is usually reported in grains of fine gold per cubic yard, which weighs about 3000 lbs., or 1½ short tons. In the panning assay, from 60 to 90 p.c. of the gold in the ore is usually recovered.

Ordinary gold ores are assayed by (1) the fusion or crucible method, or (2) the scorification method. In the *crucible assay*, the ore, crushed through an 80-mesh or finer sieve, is mixed with litharge or red lead, charcoal, or argol, and the necessary fluxes, and, fused in the melting furnace or, as in Western America, in the muffle. The amount of ore taken is usually 1 A.T. (assay-ton, see p. 319), but is sometimes only ½ A.T., and, in the case of poor tailings in which there are only a few grains of gold per ton, as much as 12 A.T. is taken and fused in several charges, the gold being finally collected into one lead button. The fluxes vary with the nature of the ore. The following are typical charges subject to very large variations to meet special cases:—

—	A. Siliceous ore (grey or white with a little pyrites, &c.)	B. Basic oxidised ore (red or brown)	C. Pyritic ore
Ore . .	1 A.T.	1 A.T.	1 A.T.
Litharge or red lead	1 „	1 „	1 „
Charcoal .	1·2–1·5 grams	2·0 grams	0–1 gram
Sodium carbonate	1½ A.T.	25 „	1 A.T.
Borax .	5–10 grams	10 „	10 grams

Sand is added to B and C if necessary for the protection of the crucible from corrosion. The borax is usually not mixed with the charge, but is added as a cover or charged in after the fusion has begun. The charge is well mixed and put into a cold crucible, which it must not make more than two-thirds full, and pieces of hoop iron or two or three tenpenny nails are embedded in the mixture. The crucible is gradually heated, a red heat beginning to appear after about 10 minutes, and a dull red heat not being attained for 30 minutes or more. Tranquil fusion results in 40 or 50 minutes from the time of charging in. The pot is then lifted out of the furnace, the nails removed, and the charge poured into a conical mould or allowed to cool in the pot, which is afterwards broken. When cool, the lead button is detached from the slag by hammering. The button should weigh at least 25 grams. If less than this amount of lead is reduced, a fresh charge is made up containing more charcoal, and any change is made in the fluxes which may seem desirable from the appearance of the slag. If the lead is hard or brittle, owing to the presence of impurities, it is usually scorified, sometimes with the addition of fresh lead, before being cupelled, as otherwise the loss of gold is increased.

The slag will contain gold and *a fortiori* silver if the conditions during fusion are favourable to oxidation of the metals. For this reason it is better to reduce almost all the litharge than to leave some of it in the slag, and the more readily oxidised metals—iron, manganese, &c.—must be reduced to their lowest oxides, ferrous oxide, &c. Practically all the copper, nickel, and other readily reducible metals will

then be in the lead button. In the case of ores containing much copper, this is a disadvantage, entailing loss of gold in cupellation, and the copper may be removed from the ore by treatment with acid before fusion (with some loss of silver) or large quantities of litharge (6 A.T. of PbO to 1 A.T. of ore) may be added, and only a small part of it reduced. In the latter case the slag contains gold and silver, and is cleaned by a second fusion, with the reduction of more lead. A similar method of fluxing is used for telluride ores, an excess of litharge in the slag preventing tellurium from entering the lead button. Antimonial and arsenical gold ores are sometimes roasted with coal-dust in a reducing atmosphere, in order to remove the antimony or arsenic as a sulphide before fusion. An alternative method is to fuse with much litharge and enough nitre to oxidise the antimony with the formation of antimoniates. Sulphides may be roasted in air before fusion.

The lead button, rounded by hammering, is placed on a hot cupel in the muffle (*see* p. 317), which is kept at a full red heat. The lead melts and oxidises, and the litharge and other oxides are absorbed by the cupel, the gold and silver being left as a bead (or 'prill') on the surface. If the bead is large and contains much silver, it must be cooled gradually to prevent it from 'spitting' on solidification, by which part of the metals might be lost. The bead is cleaned, weighed, flattened, and parted by dissolution in boiling nitric acid in a porcelain crucible or test-tube. If less than two parts of silver are present to one of gold, the metals are not parted completely, silver being left in the gold, and it is convenient to have a greater proportion of silver present. It is, therefore, often necessary to melt the bead with more silver, the proportion varying with the size of the bead, as follows:—

Weight of gold		Silver required for parting
10 milligrams		40 milligrams
1 „		6 „
0·2 „	or less	2 „

A little extra silver is permissible, but if too much silver is present, there is a tendency for the gold to break up into very fine particles, which are difficult to wash without loss. The separation of these minute particles is avoided by dropping the bead into boiling acid, sp.gr. 1·2, when the parting will be completed in a few seconds. The parted gold is washed free from silver nitrate, &c., and is made firm and coherent for weighing by being annealed at a red heat. (For weights, balances, &c., *see* p. 318.) The silver is estimated by difference. The litharge, fluxes, &c., must be tested for silver and gold by running blank charges without ore.

In *scorification* about 0·1 or 0·2 A.T. of ore is mixed with 30 or 40 grams of granulated lead, and transferred to a dry scorifier (see Fig. 5). The charge is covered by a similar amount of granulated lead, and from 0·5 to 1 gram of borax is sprinkled on last. The scorifying dish is then charged into a muffle, which has been raised to a temperature of 1000°–1100°, or considerably above that required for cupellation, and the muffle is closed. As soon as the charge is melted down, the muffle is opened. The lead now oxidises, and the litharge, forming a ring of slag round the scorifier, oxidises the sulphides, &c., and slags off the earthy materials in the ore. As oxidation proceeds, the litharge encroaches on the 'eye' of metal, and at length covers it over. A pinch of charcoal powder is then added in tissue paper, and when the fusion is again tranquil, the charge is poured into a mould, and the slag detached. The lead is cupelled, and the assay finished as before.

In cupellation some gold and silver is carried into the cupel with the litharge, especially if tellurium, selenium, copper, &c., are present. The gold and silver are usually recovered by fusing the crushed cupel with litharge, charcoal, sodium carbonate, borax, and fluorspar, and cupelling the button of lead (see Lodge's Notes on Assaying, 112–169).

Assay of gold bullion and alloys. A piece of the metal to be examined is adjusted by cutting and filing to correspond in weight with a standard weight marked '1000,' which varies with different assayers between 5 and 10 grains, but is usually 0·5 gram. To the assay piece is added a piece of silver (free from gold) equal in weight to 2½ times (at the Royal Mint 2·1 times) that of the gold estimated to be present in the alloy, which, if not already known, can be ascertained by a rough preliminary assay or by the touch-stone (*see* p. 324). The whole is wrapped in sheet lead, the weight of which depends mainly on the amount of copper to be removed, and varies from 8 to 32 times the weight of metal taken for assay. The lead packets are then transferred by means of tongs to cupels already raised to a bright red heat in the muffle, the current of air through the muffle is carefully regulated and the heat maintained. In from 10 to 20 minutes, a rapid passage of brilliant iridescent bands of colour over the surface of the button is observed to take place, and the buttons then appear to become colder, no longer glowing brightly with the oxidation of the lead. A few minutes later the muffle is closed to allow the buttons to set without loss by spitting. If copper is present in the assay pieces, however, this is not to be feared, and the charge can be drawn while the buttons are still molten. At the Royal Mint a charge consists of 72 assay pieces, which are charged in simultaneously by means of a divided metal tray with a sliding bottom and withdrawn simultaneously while still molten by means of a tray made of a mixture of graphite and clay, on which the cupels are placed. The buttons are cleaned by brushing, flattened on an anvil, annealed in the muffle or before a blowpipe, and reduced to a thickness of about 0·2 mm. by passage through a small pair of flatting rolls. The 'fillets' are again annealed and coiled into a spiral or 'cornet' by the finger and thimb.

The parting in nitric acid is effected either in glass parting flasks or in a platinum boiling apparatus. If parting flasks are used, an amount of about 2 oz. of nitric acid of sp.gr. 1·2 is heated in the flask almost to boiling, and the cornet is then dropped in and boiled until 2 or 3 minutes after the red fumes have disappeared. The acid is then poured off, and the gold, after being washed twice with boiling water, is boiled for a further 15 minutes with nitric acid of sp.gr. 1·2 or stronger. The acid must be free from silver, chlorine, &c.

The gold is again washed, and is then transferred to a porous crucible or 'annealing cup'

by filling the flask with water, placing the cup over its mouth, and inverting it. The gold falls into the cup, and the flask is removed without agitating the water in the cup. The gold is then dried, annealed by heating to redness, and weighed. If no more than three parts of silver are present to one of gold, the cornet does not break up; and if enough is known previously of the composition of the bullion to make sure of this in the cupelled button, a platinum tray, containing a number of little platinum cups may be used. A cornet is placed in each cup, and the whole tray is immersed in nitric acid, and subsequently washed by dipping in and out of hot water. Less acid is used per assay piece by this method, and the boiling is more prolonged, 30 minutes in each of two acids of sp.gr. 1·23 being used at the Royal Mint.

In each batch of assays, two or more check assays on pure gold are made to determine the 'surcharge' or net sum of the losses of gold and the gain in weight due to the retention of silver. With alloys boiled separately in flasks, check assays are of comparatively little value (see Rose's Metallurgy of Gold, 5th ed. 470–498).

Alloys of gold and silver If the alloy contains enough silver to be parted by nitric acid, no difficulty arises. The silver is dissolved, precipitated by hydrochloric acid, and weighed either as chloride or as metal. If the silver is deficient in quantity, the alloy is melted with two and a half times its weight of cadmium under a cover of potassium cyanide and parted with nitric acid. The silver is precipitated and weighed as chloride. The gold residue is annealed and weighed. Sometimes the silver is determined by difference, the alloys being cupelled and weighed, and subsequently cupelled again with the addition of silver, and parted.

(For alloys containing *gold and platinum*, see p. 327.)

Assay by the touchstone. This ancient method consists in comparing the colour of the streak produced by a sample of gold of unknown composition on a black surface with those from a series of known compositions, after all have been treated alike with nitric acid. Any abrading surface on which the acid is without action can be employed for this purpose.

Iridium occurs alloyed with platinum, and finds its way into gold bullion. In the latter case, it is found with the gold cornet obtained in the bullion assay, adhering in the form of black scales or powder to that side of the gold which was originally nearest to the cupel. It can be estimated by dissolving the gold in *aqua regia*, the iridium remaining undissolved.

Iron. The dry assay of iron, made by fusing ores with fluxes in carbon-lined (brasqued) crucibles, is obsolete, and need not be described. The wet methods are volumetric, based on the oxidation of iron from the ferrous to the ferric state or on the converse reduction. Either the bichromate or the permanganate method is generally used to determine the total amount of iron in ores or the amount of iron present in the ferrous condition. The stannous chloride method is used for measuring the amount of iron present in the ferric state in an ore.

For the determination of the total amount of iron, the ore is passed through an 80-mesh sieve, and attacked by acids as usual. Most ores are oxides, carbonates, &c., and the iron in them is easily dissolved by hydrochloric acid.

Titaniferous ores are fused with acid potassium sulphate and dissolved in water and hydrochloric acid. If nitric acid is present in the acid solution, it is destroyed by evaporating to dryness with hydrochloric acid and taking up with hydrochloric acid and water, and the iron is then reduced by zinc, which gives a stream of hydrogen or (if titanium is present) by crystals of sodium sulphite in a neutral or slightly acid solution. As soon as the solution is colourless, the excess of zinc is removed, or the sodium sulphite decomposed by boiling with hydrochloric acid, and titration is carried out in a porcelain basin by means of a solution prepared by weighing out 4·39 grams of potassium bichromate to the litre, equivalent to 5 grams of iron according to the equation:

$$6FeCl_2+K_2Cr_2O_7+14HCl = 3Fe_2Cl_6+Cr_2Cl_6+2KCl+7H_2O.$$

Potassium ferricyanide (0·1 p.c. solution, freshly prepared) is used as an indicator, a drop from the assay solution being mixed with a drop of the test solution on a white glazed tile, from time to time. The end-point is reached when a colour is no longer produced. The solution of bichromate is standardised by means of piano wire, which contains about 0·4 p.c. of impurities.

The permanganate method is carried out in a sulphuric acid solution, the equation being:

$$10FeSO_4+K_2Mn_2O_8+8H_2SO_4 = 5Fe_2(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

The standard solution is prepared by weighing out 2·82 grams of potassium permanganate per litre, which is equivalent to 5 grams of iron. The end reaction, the appearance of a pinkish tinge in the solution in the flask, is very sharp.

When the amount of ferrous iron only in the ore is required, the ore is dissolved in hydrochloric or sulphuric acid with exclusion of air. The ferric iron may be determined by difference, or, as a check, the stannous chloride method may be used, in which the yellow solution of ferric iron in hydrochloric acid is decolourised. The standard solution (20 grams of commercial stannous chloride per litre, acidulated with hydrochloric acid) is run into a boiling-hot solution of iron, and is standardised by means of a solution of ferric chloride free from nitric acid.

Analysis of iron and steel. The elements requiring estimation are carbon (graphite, combined carbon and total carbon), *silicon*, manganese, sulphur, phosphorus, arsenic, and, in special steels, chromium, nickel, tungsten, molybdenum, vanadium, &c. The total carbon is estimated by combustion, usually after removal of the iron by a cupric salt. The graphite is estimated by combustion of the residue after dissolving the iron in hydrochloric acid, by which the combined carbon is removed in combination with the hydrogen evolved, or more advantageously in nitric acid, by which the combined carbon is oxidised and retained in solution. The combined carbon is determined by the colour of a nitric acid solution compared with the colour of certain standard solutions containing known amounts of carbon. Silicon is weighed as silica after dissolution of the iron by acids or iodine. Sulphur is weighed as

barium sulphate, after the iron has been dissolved in *aqua regia*, or it is evolved as sulphuretted hydrogen, which is absorbed by caustic soda, and decomposed by a standard solution of iodine. The excess of iodine is estimated by sodium thiosulphate.

Manganese is separated by precipitation with bromine in an ammoniacal solution after removal of the iron as basic acetate. The precipitated hydrated peroxide is heated strongly in a muffle and weighed as Mn_3O_4. There is also a colorimetric estimation, the steel being dissolved in nitric acid and the solution boiled with lead peroxide. The colour of the permanganate produced is compared with those of standard solutions. Phosphorus is precipitated by ammonium molybdate or magnesia mixture. Arsenic is separated by precipitation as sulphide in an acid solution, converted into arsenic acid and determined by precipitation by magnesia mixture.

(For the determination of the metals in special steels, *see* under the headings *Chromium*, *Nickel*, &c. For full details of the analysis of iron and steel and also of the complete analysis of iron ores, *see* Blair's Chemical Analysis of Iron, Campredon's Guide Pratique du Chimiste Métallurgiste et de l'Essayeur, 438–634, and Brearley and Ibbotson's Analysis of Steel Works Materials.)

Lead. Both dry and wet methods of assay are used. The dry assay is only applicable to rich ores and to concentrates, and even with these is less accurate than the wet methods. The ore is crushed through a 60-mesh sieve, mixed with sodium carbonate and argol, and fused in a wrought-iron crucible or in a clay pot with hoop-iron. Galena is reduced by the iron, and any oxides, sulphates, &c., of lead are reduced by the argol. Borax is sometimes added as a cover. The following are examples of the charges recommended by Percy:—

	1. Rich galena	2. Any galena, poor ores	3. Phosphate ore	4. Cerussite
Ore . .	500 grs.	500 grs.	300 grs.	500 grs.
Sodium carbonate .	500 „	350 „	350 „	500 „
Argol (tartar)	50 „	100 „	100 „	100 „
Borax . .	—	150 „	30 „	30 „

The iron crucible is made red hot, cleaned, and allowed to cool. The charge is then transferred to it, care being taken to avoid loss by dusting, and the borax, or, if none is used, part of the sodium carbonate is added as a cover. A clay lid is also placed on the crucible. The charge is slowly heated for about 20 minutes, and is then poured into a mould, provided that all signs of effervescence have disappeared, and the mixture is seen to be in a state of tranquil fusion. The lead is found at the bottom. It is detached from the slag with a hammer, and is cleaned and weighed. The slag is examined for lead beads before being thrown away. Clay crucibles are used for phosphate and carbonate ores.

When the ore contains arsenic, a speise is formed which is found adhering to the upper surface of the lead, below the slag. It must be removed with great care to avoid loss of lead. The lead should be soft and malleable. The silver and gold in the ore are determined by cupellation and parting (*see* p. 323). The method gives results with pure ores which are about 1 or 2 p.c. too low. When the ore contains antimony, bismuth, copper, &c., these metals are in part reduced with the lead, and are weighed with it. If the lead button is hard, it is necessary to estimate the lead in it by weighing it as lead sulphate or otherwise, or to adopt wet methods of assaying the ore.

(For details of the dry assay of lead, see Percy's Metallurgy of Lead, 103–119.)

In the wet methods, oxidised ores are attacked by hydrochloric acid, followed by nitric acid, if necessary. Sulphide ores are treated direct with nitric acid. The lead is determined either as sulphate or volumetrically, by means of ammonium molybdate (Alexander's method). In the latter method (Eng. and Mng. J. April 1, 1893, 298), the mixture of nitric acid and ore is evaporated with sulphuric acid, diluted, boiled, and filtered. The lead sulphate in the residue is dissolved in hot ammonium acetate, acidified with acetic acid, raised to boiling, and titrated with a standard solution of ammonium molybdate, containing, according to Low, 4·25 grams per litre. The solution is standardised with pure lead foil. Tannin is used as an indicator, giving a yellow colour to a drop of the solution ou a white glazed tile when the ammonium molybdate is in excess. If iron and calcium are present, it is better to separate the lead as sulphide and redissolve before titration (Low's Ore Analysis, 113).

Lead may also be determined in a feebly acid solution by adding an excess of potassium chromate and estimating the amount of excess by means of a standard solution of ferrous chloride. The reaction is the same as in the bichromate assay of iron, but in this case the end is marked by the appearance of a green colour in the test drops on the plate (Beringer's Assaying, 214).

Manganese occurs as MnO_2 in pyrolusite, when the value of the ore usually depends on its property of liberating chlorine when heated with hydrochloric acid, and not on the proportion of metal contained in it. Nevertheless, the percentage of manganese in ores is sometimes required, and spiegeleisen, ferromanganese, and steel are also assayed for manganese. Either the ferrous sulphate assay or Volhard's volumetric process is generally used. In the latter method, the manganese is precipitated by potassium permanganate in a boiling neutral solution. The precipitate, as far as numbers are concerned, is represented by the equation:

$$K_2Mn_2O_8+3MnSO_4+2H_2O = K_2SO_4+5MnO_2+2H_2SO_4.$$

About one gram of the ore or spiegeleisen is dissolved in hydrochloric and nitric acids, heated with sulphuric acid, and neutralised by the addition of an emulsion of zinc oxide in slight excess. All the iron is precipitated, and, after violently shaking the mixture, it is made up to 500 c.c., allowed to settle, and 100 c.c. of the clear supernatant liquid is drawn off, heated to boiling, and titrated. The end point is marked by the appearance of a pinkish tinge. (For the estimation of manganese in steel, *see* above.)

Mercury. The wet methods of assay are not satisfactory, and one of the distillation methods is usually employed. When a large percentage

of mercury is present, a combustion tube of 18–20 inches long is used. It is sealed at one end and magnesite powder placed in it first, to a depth of 3 or 4 inches. Next a layer of 2 inches of unslaked lime is added and then 5 or 10 grams of ore well mixed in a mortar with 10 grams of lime. The mortar is cleaned with more lime and the rinsings added to the tube and covered with clean lime to a depth of 3 or 4 inches. Finally, a loosely fitting plug of asbestos is inserted and the unoccupied portion of the tube is drawn out almost to a point and bent over at right angles, care being taken that no hollow in the glass is formed which might collect some of the mercury. The tube is placed in position in a combustion furnace and tapped until the mixture settles and leaves a free passage for gases throughout its length. The narrow opening is made to dip into a beaker of water, and the tube is heated, beginning with the asbestos plug and finishing with the magnesite, which yields enough carbon dioxide to sweep out the vapours of mercury. The time required for heating is about 30 minutes. While the tube is still red hot throughout its length, its end is cut off and dropped into the beaker. The mercury collects in the water, and is dried by blotting-paper and then in a desiccator and weighed in a porcelain crucible.

When only small quantities of mercury are present, Eschka's method is used (Dingl. poly. J. cciv. 74), in which the mercury is condensed on a weighed piece of gold. This is in the form of a basin made of thin sheet gold, used as the cover of a porcelain crucible and filled with water to keep it cool. The basin projects beyond the rim of the crucible, and usually weighs about 10 grams. From 0·2 to 2·0 grams of ore is mixed with 1–4 grams of iron filings, and heated in the crucible for 10 or 20 minutes, the flame being kept from heating the upper part. This may be done by fitting the crucible into a hole in a piece of sheet asbestos. The gold basin is then dried without the agency of heat, and weighed, the increase of weight representing the mercury.

Molybdenum in ores is estimated by precipitation as mercurous molybdate in a very slightly alkaline or neutral solution by means of mercurous nitrate. The precipitate is ignited in a porcelain crucible, either alone or with litharge, until the mercury is expelled. The increase in the weight of the crucible is taken as MoO_3, but if chromium, vanadium, tungsten, phosphorus, or arsenic is present in the ore, the ignited MoO_3 must be purified by further treatment or separated before precipitation. Molybdenum in steel is precipitated as ammonium phospho-molybdate.

Nickel and **cobalt** occur together in ores, the former more commonly and in greater proportion than the latter. They are usually assayed together. In the fire assay, the ore is roasted sweet and then fused with arsenic to form a speise. This is heated in air on a little clay dish in the muffle, and the metals oxidised successively, iron passing into the slag first, cobalt next, and then nickel, copper being left until last. The changes in colour of the borax slag show the progress of the assay. The slag is coloured brown while iron is passing into it, blue by cobalt, sherry-brown by nickel, and blue by copper. Gold is added to the speise after the elimination of cobalt if copper is present. The speise is weighed after each metal has been removed. The slag must be frequently examined and renewed, and great care and experience are needed to attain even approximate results.

The method is easier to carry out if copper is absent, and this metal is sometimes removed by precipitation with sulphuretted hydrogen in an acid solution before the speise is formed. If cobalt is absent, a weighed amount may be added, as otherwise it is difficult to observe the point at which nickel begins to pass into the slag after the removal of the iron. The arsenides in the speise have the formulæ Fe_2As, Co_2As, Ni_2As, and Cu_3As (Rhead & Sexton's Assaying, 187).

In the wet methods it is usual to roast the ore as a preliminary in order to remove the arsenic, sulphur, &c., and then to separate the nickel and cobalt from the iron, manganese, zinc, &c., by suitable methods. The nickel is precipitated as hydrate and weighed as NiO. Cobalt is often included in the nickel, but is separated if present in large quantities. A volumetric method depends on the interference by nickel in the titration of cyanide with a standard solution of silver nitrate. An alkaline solution containing caustic soda is used, and a little potassium iodide added as an indicator. An excess of a standard solution of potassium cyanide is added to a solution of nickel sulphate made alkaline (and precipitated) by caustic soda. The excess of cyanide is titrated by a standard solution of silver nitrate (Beringer's Assaying, 255). The reactions are represented by the equations:

$$4KCy + NiSO_4 = K_2NiCy_4 + K_2SO_4.$$
$$2KCy + AgNO_3 = KAgCy_2 + KNO_3.$$

Nickel and cobalt are also sometimes estimated by electrolysis, and for this purpose must be separated from zinc and other metals, dissolved in nitric acid, and precipitated in an ammoniacal solution.

For the separation of nickel from cobalt, *see* J. Soc. Chem. Ind. ix. 375.

Nickel in steel is precipitated by bromine water and caustic soda, after removal of the iron as basic acetate. It is weighed as NiO.

Platinum in alluvial deposits is concentrated by panning, as in the case of auriferous sands. In all cases platinum can be collected in lead by the same methods as those described under the assay of gold ores. The lead buttons are sometimes cupelled at a very high temperature, but it is difficult to remove the whole of the lead in this way, as the 'prill' freezes on the cupel when only part of the lead has been oxidised.

Cupellation may be finished in the oxygen-gas blowpipe flame, but the loss of platinum is then large. It is more usual to dissolve the lead button in dilute nitric acid and to filter off the platinum and gold residue, which is parted by dissolving in *aqua regia*, and precipitating the gold with oxalic acid. The platinum is estimated by difference or by precipitation as $(NH_4)_2PtCl_6$.

Platinum in alloys or in rich alluvial concentrates may be estimated by melting with six parts of pure lead, and grinding in a mortar the brittle alloy freed from slag. Portions of the alloy are scorified with fresh lead and dissolved in nitric acid.

Alloys containing gold, silver, and platinum are difficult to assay, as they are insoluble in *aqua regia*. The method adopted is first to cupel the alloy to remove copper, &c., these metals being estimated by difference. The alloy is then inquarted by cupellation with twice its weight of silver and parted by boiling in sulphuric acid. The residue contains the gold and platinum. These may be parted by again inquarting with silver and dissolving in nitric acid, provided that the amount of gold present is at least ten *times* that of the platinum. If the proportion of gold present is less than this, part of the platinum remains undissolved, and it is therefore necessary to add gold in many cases. The parted gold is weighed and the platinum estimated by difference (6ème Rapport des Monnaies, 1901, p. xxix.; Rose's Precious Metals, 272).

Silver. The ores of silver are assayed in the same way as those of gold of a similar kind, the scorification method being used far more frequently than in the case of gold ores. The slags and cupels must be examined usually, as silver is more readily lost than gold. The temperature of cupellation is kept as low as possible, to check the loss of silver by volatilisation (see Lodge's Notes on Assaying, 37–111).

Silver bullion and alloys are assayed by cupellation, by the Gay Lussac or the Volhard volumetric processes, or by weighing the chloride (India Mint method). In cupellation, the 'base' or oxidisable metals are removed in the muffle, and the silver prill is cleaned and weighed. The weight of silver taken is usually 10 grains. The amount of lead required varies from six times the weight of the silver for alloys of high standard to twelve times for silver 700 fine. The method is not suitable for alloys containing less than 70 p.c. of silver. The muffle is kept at a lower temperature than that required for gold cupellation, but must be raised to above the melting-point of pure silver (962°) at the finish, to prevent the metal from setting in the furnace before all the lead has been removed. When the cupellation is complete, the mouth of the furnace is closed with great care to exclude draughts, and the furnace is allowed to cool slowly to prevent loss of silver by spitting. The solidified prills are cleaned and weighed. The loss of silver in cupellation varies from 5 to 15 parts per 1000, and check assays on pure silver are placed in all parts of the furnace to measure this loss. Any gold that may be present is weighed as silver. The process is very ancient, and clear reference is made to it in connection with a trial of the Pyx in the Black Book of the Exchequer, written in the reign of Henry II.

In the Gay Lussac process, the volume is measured of a standard solution of common salt or sodium bromide required for the precipitation of a little more than a gram of silver in solution as nitrate. No indicator is used, and the end of the operation is judged from the appearance of a faint cloud of chloride in a solution from which almost all the silver has been precipitated. It is the most accurate method of assaying silver bullion. The standard solution of common salt (usually called the 'normal solution') contains about 5·416 grams of NaCl per litre, so that 100 c.c. will precipitate 1 gram of silver. A weight of silver bullion containing about 1·003 gram of silver is weighed and dissolved in nitric acid, and 100 c.c. of the salt solution added to it from a pipette. The chloride is agglomerated by a shaking in a stoppered bottle, and the clear supernatant liquid is tested by 'decinormal' solutions of common salt and, if necessary, of silver nitrate. The appearance of the cloud of silver chloride shows the amount of silver left in solution. Further shakings are resorted to if required, and the final reading is taken after waiting for about 5 or 10 minutes. Check assays on fine silver are used with every batch to test the strength of the solution, which varies with the temperature, &c. Mercury interferes with the method, and is detected by the colour of the precipitated silver chloride, which does not darken if mercury is present. Acetate of soda corrects the error if the quantity of mercury present is small. The Gay Lussac method can be used only in cases where the approximate assay is already known (Percy's Silver and Gold, 282; Riche et Forest, L'Art de l'Essayeur, 183).

In the India Mint method, the silver alloy is dissolved in nitric acid and precipitated by a slight excess of hydrochloric acid. The silver chloride is then collected by shaking in a stoppered bottle, and, after being washed, is transferred to a porous cup, dried, and weighed while warm. The chloride is washed by decantation, but the drying is tedious, and is expedited by breaking up the crust with a glass rod. Any gold that may be present is weighed as silver chloride. This is the best method for alloys containing less than 70 p.c. of silver (Trans. Inst. Mng. & Met. xvii. 334).

The Volhard method is largely used in this country. The nitric acid solution of the silver is freed from nitrous acid by boiling, and is then diluted and titrated with a solution containing 7·04 grams of ammonium thiocyanate per litre. As this salt is deliquescent, it is usual to weigh out about 7·3 grams per litre. Iron alum is used as an indicator, giving a red colour when all the silver has been precipitated. Time is saved and the accuracy of the method increased by taking for assay an amount of alloy containing about 1·003 gram of silver, and running in 100 c.c. of the standard solution of thiocyanate from a pipette. After shaking the liquid in a flask, the titration is finished by adding the thiocyanate a drop or two at a time. Check assays on fine silver are used (Trans. Inst. Mng. & Met. xvi. 154).

Tin. Tin ore is concentrated on a vanning shovel with the production of 'black tin' in order to determine what yield may be expected when the ore is treated on the dressing floors. The ore is crushed and sampled, and about 30 grams are thoroughly mixed with 30 or 40 c.c. of water on the vanning shovel with the fingers, to prevent, as far as possible, the loss of 'float tin.' The ore is then collected by a vigorous circular motion of the water, and the slimes are poured off, a process which is repeated until the water remains clear after being left to settle for a few seconds. By means of a circular motion of the shovel, combined with a series of jerks, the tin oxide is now separated from the lighter material, which is carried down by the descending wave. The tailings are saved and washed over again until they yield no more tin,

and are then crushed by rubbing with a hammer and again washed. The concentrates are dried and roasted and dressed once more. Sometimes they are washed quite clean from worthless material, and sometimes left impure with oxide of iron, &c., according to the nature of the ore and the custom of the operator. Sometimes they are purified by boiling in hydrochloric acid or *aqua regia*, which, according to J. H. Collins, causes a loss of tin. The residue is usually reported in pounds of black tin to the long ton of ore, or alternatively in parts per 200, so that a produce of '9½' would be equivalent to 4·75 p.c. (Beringer's Assaying, 276).

The black tin obtained by vanning is assayed for metallic tin by reduction with anthracite (Cornish method) or potassium cyanide. In the Cornish method 100 grams of tinstone are heated with 20 grams of anthracite in a plumbago crucible at a white heat for 15 or 20 minutes. The charge is then stirred with a stick and again heated for a few minutes before pouring. The excess of anthracite contains beads of tin, which are separated by vanning. In the cyanide process, 10 grams of tinstone are fused with 40 grams of impure cyanide (containing potassium carbonate), and poured at a red heat. The German process consists in reducing a mixture of 5 grams each of tinstone and cupric oxide with 15 grams of black flux (a mixture of carbon and potassium carbonate, obtained by heating tartar) and 1·25 grams of borax with a cover of common salt. The reduced metal is compared in weight with that of the copper reduced from cupric oxide alone. The most trustworthy of these methods is the fusion with cyanide. The reduced tin, however obtained, is usually impure (Beringer's Assaying and Kerl's Metallurgische Probirkunst).

A good wet method for the estimation of tin in ores without previous concentration is described by G. L. Mackenzie (Trans. Inst. Mng. and Met. xiii. 1904, 87). It consists in cleaning a sample of from 1 to 5 grams of the ore with *aqua regia* (and removing the tungstic acid, if it is present, by means of ammonia), reducing the stannic oxide to tin by ignition in a current of coal gas, dissolving the metallic tin with hydrochloric acid and potassium permanganate, precipitating with sulphuretted hydrogen, and igniting the tin sulphide. The tin is weighed as stannic oxide.

Tin is also estimated volumetrically. A satisfactory method described by Beringer (Text-Book of Assaying, 11th ed. 285) is to reduce the solution of stannic chloride to stannous chloride by means of nickel foil, and to titrate with a standard solution of iodine in an atmosphere of carbonic acid gas. Starch is used as an indicator. In all wet methods, tin oxide must be reduced to metallic tin before it can be dissolved.

Titanium in ores is generally in the form of titanic oxide, which is insoluble in acids. Titanates, however, are somewhat soluble, so that on attacking ores with acid, titanium will be found partly in the residue and partly in the solution. The metals of the iron group with titanium are precipitated from the solution as basic acetates, which are fused with potassium bisulphate and extracted with water. The titanic acid is precipitated from the solution by means of prolonged boiling with sulphurous acid. The residue left by the attack on the original ore with acids is similarly treated, after the silica has been removed by heating with sulphuric and hydrofluoric acids (Beringer's Assaying, 293).

Tungsten in wolfram, steel, &c., is estimated by weighing as tungstic acid WO_3. The ore is boiled with hydrochloric acid or *aqua regia*, when the tungsten separates as insoluble yellow tungstic acid. After thorough washing, this is dissolved in ammonia, filtered, and recovered by evaporating the solution to dryness, and gently igniting the residue to decompose the ammonium tungstate. Nearly pure tungstic acid remains. Any silica that may be present may be removed by hydrofluoric acid.

Uranium. The mineral is evaporated with nitric acid and taken up with HCl. After separation of the other metals as sulphides and carbonates, the uranium is precipitated by ammonia and weighed as U_3O_8, or it is precipitated by microcosmic salt in the presence of acetic acid and ammonium acetate. The precipitate consists of ammonium uranyl phosphate $UO_2NH_4PO_4$ which is washed, ignited gently and weighed or converted into uranyl pyrophosphate $(UO_2)_2P_2O_7$, for greater accuracy (Low's Technical Ore Analysis, 201). This precipitation is also the basis of a volumetric method, a boiling solution of uranium being titrated with a standard solution of phosphate, until ferrocyanide no longer gives a brown colour.

Vanadium in steel is estimated by titrating with potassium permanganate. The steel is dissolved in HCl and evaporated to dryness with a little nitric acid. The residue is fused with nitre and fusion mixture, boiled in water and filtered, and the filtrate evaporated with H_2SO_4, reduced by sulphur dioxide and titrated. One atom of iron is equivalent to one of vanadium in the titration (Rhead and Sexton's Assaying, 270).

Zinc. The old dry methods of assay of ores and alloys based on the loss of weight due to the volatilisation of zinc at a white heat are obsolete. Zinc is usually weighed as oxide after precipitation as carbonate, or it is titrated with sodium sulphide or potassium ferrocyanide. An amount of 1 or 2 grams of ore is weighed out and dissolved in hydrochloric acid or *aqua regia*. The silica and metals other than zinc are removed as usual. All the precipitates will contain zinc if they are bulky, and must be redissolved and reprecipitated. The alkaline filtrate may be diluted to 200 c.c. and used for the sodium sulphide titration, which is carried out at 50°–60°. A flake or two of freshly precipitated ferric hydrate is used as an indicator, turning from red to black as soon as sodium sulphide is in excess. One c.c. of the standard solution of sodium sulphide should be equal to 0·01 gram zinc. Instead of ferric hydrate, sodium nitroprusside may be used as an indicator on a white tile. This gives a purple colour with sodium sulphide.

For titration with potassium ferrocyanide, the pure ammoniacal solution of zinc obtained as above is acidified with hydrochloric acid, boiled and titrated hot. The standard solution of ferrocyanide is made up by dissolving 41·25

grams of the pure salt in a litre of water. The test solution consists of 0·5 gram of uranium acetate dissolved in 20 c.c. of water. A drop of this solution gives a brown colour on a white tile with a drop of the zinc solution as soon as the ferrocyanide is in excess. It is advisable to confirm the end reaction by adding 5 c.c. of a standard solution of zinc in hydrochloric acid, containing 10 grams of zinc per litre, and again titrating (Chem. News, lxxvi. 6).

The assay of zinc-dust for metallic zinc is made by acting on the sample with dilute sulphuric acid, and collecting and measuring the hydrogen which is evolved.

Commercial metallic zinc contains lead, cadmium, and iron, and may also contain arsenic, copper, antimony, tin, &c. By dissolving in dilute sulphuric acid, the lead and the greater part of the copper, tin, cadmium, &c., are left undissolved. The residue is attacked by nitric acid, and the metals separated as usual. Iron in zinc is titrated in the sulphuric acid solution without being separated. Arsenic and antimony are passed with the hydrogen evolved by sulphuric acid into a solution of silver nitrate (Campredon, Guide Pratique, 760; Eliot and Storer, Amer. Acad. Arts & Sciences, viii. 57).

Coal. The assay of coal usually comprises the determination of moisture, total ash, sulphur, coking properties, and calorific power. The coal is broken down and sampled as in the case of ores (see p. 316), and the sample is passed through an 80-mesh sieve.

The moisture is determined by drying 1 gram in a water-oven for 30 minutes and weighing. The coal is then again warmed for 15 minutes and reweighed, and the process is continued until the weight is constant or begins to increase.

For sulphur, 2 grams of coal are mixed with 3 grams of a mixture of two parts of calcined magnesia and one part of potassium carbonate, and heated to dull redness for an hour in a porcelain or platinum crucible, with occasional stirring. After cooling, the charge is transferred to a beaker and digested with water and 1 c.c. of bromine. It is then acidulated with hydrochloric acid, the bromine boiled off, and the sulphur, now in the form of sulphate, precipitated by barium chloride. The sulphur may also be oxidised by heating the coal with a mixture of nitre and common salt. Phosphorus in coal, if determined at all, is estimated in the ash, which may require complete analysis.

The coking qualities of coal are examined by heating 50 grams of coarsely crushed coal in a 'large copper' crucible covered with a closely fitting lid. The evolution of gases is completed after 15 or 20 minutes at a full red heat. After cooling, the coke is turned out and weighed, the loss of weight giving the amount of volatile matter.

The calorific power of coal is determined by igniting 2 grams of the finely powdered sample with 20 grams of a mixture of six parts of potassium chlorate and one part of nitre. The coal and deflagrating mixture are ground together in a mortar and ignited in a Thompson calorimeter. The error due to loss of heat by escaping gases, &c., is always taken as one-tenth of the total evolved. The calorific power reported is the weight of water that could be evaporated at 100° and 760 mm. pressure by a unit weight of the fuel (*v.* FUEL).

Cyanide solutions. In gold mills, these solutions are in wide use, and require frequent analysis. Free cyanide is estimated by means of a solution of silver nitrate prepared by dissolving 13·04 grams of crystallised $AgNO_3$ in a litre of water. One c.c. of this solution is equivalent to 0·01 gram of KCy, the end of the titration being denoted by the solution becoming milky from the precipitation of AgCy. The reaction is represented by the equation:

$$AgNO_3+2KCy=KAgCy_2+KNO_3.$$

The amount of cyanide solution taken for assay may be from 10 c.c. to 100 c.c., according to its strength. Alkalis and other compounds which may be present dissolve silver cyanide, and accordingly it is usual to add potassium iodide as an indicator. Turbid cyanide solution must be filtered before titration. If soluble sulphides are present, they prevent the assay from being carried out. They are removed by agitating the solution with freshly precipitated lead carbonate. If zinc is present in the solution, part of the cyanide contained in the double cyanide K_2ZnCy_4 is estimated as free KCy.

The 'total alkali' in a cyanide solution is estimated (J. E. Clennell, Chemistry of Cyanide Solutions, 62) by titration with a standard solution of sulphuric acid, using methyl orange as an indicator. 'Protective alkali' (*op. cit.* 63) is determined by adding a slight excess of silver nitrate together with a little phenolphthalein solution, and titrating with sulphuric acid until the pink colour disappears. The 'reducing power' of cyanide solutions is determined by acidification and subsequent titration with potassium permanganate, until the pink tint becomes permanent, or by adding an excess of permanganate followed by an excess of potassium iodide and estimating the amount of iodine liberated (*op. cit.* 71).

Gold and silver in cyanide solutions are determined by evaporation on lead foil, which is afterwards cupelled, or by evaporation with litharge, which is fused for lead. A more rapid method is to precipitate the gold and silver with zinc-dust and sulphuric acid, filter, and scorify or fuse the residue. The latter method is especially suitable for treating large samples of poor solutions containing very little gold and silver. In all these methods, a button of lead is obtained which is cupelled and the gold and silver parted as usual.

Silica. The silica in ores is partly free and partly combined. The white sandy residue left after careful extraction with acids is sometimes nearly pure silica, and is often reported as 'silica and *silicates insoluble in acids.*' It may be tested with sulphuric and hydrofluoric acids. The usual method with ores, slags, &c., is to fuse 1 gram with 5 grams of fusion mixture and a little nitre in a platinum crucible or dish. It is extracted with warm water and a little hydrochloric acid and evaporated to dryness on a water-bath. The bases are dissolved out with hydrochloric acid, and the silica filtered off. The filtrate is again taken to dryness and dissolved in hydrochloric acid to separate the remainder of the silica. If the ore contains a

large percentage of sulphides, oxides, &c., which are soluble in acids, these are removed before the fusion. In this case the acid solution may contain silica, which is removed by evaporating to dryness, taking up with hydrochloric acid and filtering. The purity of the silica is tested by evaporating two or three times with water, sulphuric acid and hydrofluoric acid. The silica is volatilised (J. Amer. Chem. Soc. xxiv. 1902, 362).

Sulphur. A rapid method of determining the sulphur in ores given by Furman (Manual of Practical Assaying, 5th ed. 91) is to fuse 5 grams of the ore with 15 grams of borax, 3 grams of charcoal, and one or two nails in a hot fire. The time required for fusion is about 15 minutes. The nails are then withdrawn and the charge poured. As soon as the slag is cool, the matte is detached from it with a hammer and weighed. If the matte were pure FeS, it would contain 36·3 p.c. of sulphur. By analysis, Furman finds that the nearest approximation is to take the sulphur as 30 p.c. of the matte. The method, though inaccurate, is sometimes useful, as it can be completed in less than half an hour.

The more accurate methods consist in oxidising the sulphur by *aqua regia* or nitric acid and potassium chlorate, or by fusion with a mixture of nitre and sodium carbonate, and weighing it as barium sulphate. A good method for ores and slags consists in fusion with caustic alkali, extracting with water, and oxidising with bromine. After separation of the silica, the sulphur is precipitated by barium chloride (Chem. News, l. 1884, 194). If lead is present, the solution is boiled with ammonium carbonate. T. K. R.

ASTATKI. A Russian term, signifying 'dregs,' applied to the residue left in the distillation of Baku petroleum after the volatilisation of the kerosene, and now largely used as fuel in the Caspian region (*v.* PETROLEUM).

ASTERIA (*Star Sapphire*) *v.* CORUNDUM.

ASTRALINE. Russian petroleum oil, used for burning (*v.* PETROLEUM).

ASTRALITE. A glass resembling aventurine, but containing crystals of a cupreous compound which by reflected light exhibit a dichroic iridescence of dark red and greenish blue. Made by fusing and allowing to cool slowly a mixture of 80 pts. silica, 120 lead oxide, 72 sodium carbonate, 18 borax, with either 24 pts. scale oxide of copper, and 1 pt. scale oxide of iron, or with 5 pts. lime, 26 copper oxide, and 2 iron oxide.

ASTROLIN. Trade name for antipyrine-methyl-ethyl glycollate $C_5H_{10}O_3,C_{11}H_{12}ON_2$, m.p. 64°–65·5°. A colourless powder, with a slight smell and pleasant taste, readily soluble in water and alcohol.

ASUROL. Sodium-mercuri-amido-oxy*iso*-butyrosalicylate.

ASYPHIL. Trade name for a *mercury salt of p-aminophenylarsinic acid*

$$(NH_2C_6H_4AsO(OH)O)_2Hg.$$

(*v.* ARSENIC, ORGANIC COMPOUNDS OF; *cf.* p. 337).

ATACAMITE. Hydrated oxychloride of copper $CuCl_2{\cdot}3Cu(OH)_2$, occurring in the Atacama region of Chile, sometimes in sufficient amounts for use as a copper ore (Cu 59·4 p.c.). Large quantities have also been mined at Wallaroo in South Australia. Orthorhombic crystals of a bright-green colour and with brilliant faces are not uncommon. Sp.gr. 3·76. Before the days of blotting-paper, it was used, under the name of arsenillo, as a writing sand for absorbing ink (*v.* COPPER). L. J. S.

ATELESTITE. A bismuth arsenate containing iron phosphate found at Schneeberg in Saxony: Bi_2O_3, 57·15; $Fe_2P_2O_6$, 12·50; As_2O_3, 30·35 (Freuzel, J. M. 1873, 785).

ATHAR or **ATTAR.** Indian name for volatile oil of roses (*v.* OILS, ESSENTIAL).

ATLAS DYNAMITE *v.* EXPLOSIVES.

ATLAS POWDER *v.* EXPLOSIVES.

ATLAS SCARLET *v.* AZO- COLOURING MATTERS.

ATMOSPHERE. The gaseous envelope surrounding any liquid or solid body; more particularly the gaseous envelope which surrounds the earth, and which is commonly known as air. The thickness of this aërial envelope is not known even approximately, but it is quite certain that it exceeds 45 miles measured from the earth's surface, which was the limit assigned to it by Wollaston. Secchi calculated that air exists even at a height of 300 kilometres above the earth's surface. From the ratio of decrease of density with elevation, the atmosphere at a height of 50 miles cannot exert any measurable pressure. The mass of the atmosphere forms, like the earth itself, an oblate spheroid, the polar axis of which is much shorter than the equatorial axis, the ratio of the two axes being, according to Laplace, as 2 to 3.

The pressure of the atmosphere at any particular spot may be measured in terms of the height of a column of mercury which it is capable of sustaining. It follows from the law of Boyle, that the density of the air rapidly diminishes with the height. For air of constant temperature, its density, or, what comes to the same thing, the height of the mercurial column, should diminish in geometric progression, whilst the distance from the earth increases in arithmetic progression. The pressure, even at the same place, is continually varying from a variety of causes, and hence the height of the barometer, as the mercurial column was first termed by Boyle, is practically never absolutely constant. The average height at any one spot at the sea-level is mainly dependent upon the great movements of air which result from the effect of the earth's motion upon the gaseous envelope, combined with variations in the density of the aërial mass due to solar action.

According to Regnault, 1 litre of dry air, free from carbonic acid and ammonia, measured at 0° and 0·76 mm. pressure, at Paris (lat. 48° 50′) and at a height of 60 metres above the sea-level, weighs 1·293187 grams. Lasch found that 1 litre of pure air at standard temperature and pressure weighs at Berlin (lat. 52° 36′) 1·293635 grams.

The Bureau Internat. des Poids et Mesures adopts for the weight of 1 litre of dry air, containing 0·04 p.c. carbonic acid, at the normal temperature, and under the normal barometric pressure at lat. 45° and sea-level,

$$P_{t,t} = \frac{1{\cdot}293052}{1+0{\cdot}00367} \times \frac{1}{760},$$

on the assumption that 0·00367 is the expansion coefficient of air at constant pressure for a normal degree. For purposes of ordinary chemical calculation it may be assumed with

sufficient accuracy that 1 gram of air measures 773 c.c. at standard temperature and pressure.

The total weight of the atmosphere is about 11 trillions of pounds, or about 5 trillion kilograms and the relative amounts of the chief constituents may be assumed to be—

	Trillions kgm.
Nitrogen (argon, &c.)	4·041200
Oxygen	1·218040
Carbonic acid	0·003156
	5·262396

Herschel calculated that, allowing for the space occupied by the land above the sea, the mass of the atmosphere is about $\frac{1}{1200}$ part of that of the earth.

The unit of pressure adopted by engineers and others, and styled an *atmosphere*, is an amount equal to the average pressure of the atmosphere at the sea's level. In British measure an atmosphere is the pressure equivalent to 29·905 inches of mercury at 32°F. at London, and is about 14·73 lbs. on the sq. inch. In the metric system it is the pressure of 760 mm. (29·922 inches) at 0°C. at Paris, and is equal to 1·033 kilos. on a sq. centimetre. Hence the English 'atmosphere' is 0·99968 that of the metric system.

The specific heat of air at constant pressure is 0·2374 (Regnault). Its coefficient of thermal expansion between −30° and 200° is 0·003665 for 1°.

By the application of sufficient cold and pressure, air may be liquefied.

Comparatively little of the sun's heat is absorbed in its direct passage through the air. According to Tyndall, a column of air 1 metre long absorbs 0·088 p.c. of the heat which passes through it. According to Violle, and also Lecher and Pernter, the amount is not greater than 0·0070 p.c. This absorption is mainly due to aqueous vapour, and, in a lower degree, to carbonic acid and suspended organic matter. The air mainly gets its heat by conduction from the earth, and hence, as a rule, it is hottest near the ground. The law of the decrement in temperature corresponding to height is not accurately known; it is usually stated to be about 0·56° per 100 metres, but the rate is liable to very great variations.

Air is not perfectly transparent. Its particles reflect and scatter light in sufficient quantity to obscure the light from the stars. The blue colour of the sky is due to the fact that the most refrangible rays are most widely scattered. In the higher regions of the atmosphere, where the amount of reflected light becomes less and less, owing to the decreased density of the air, the sky appears to grow gradually darker. Brewster first proved that the blue light from the sky, as well as the white light from the clouds, was due to reflected light, by the fact that it was polarised.

Suspended matter, dust, smoke, aqueous vapour in a state of partial precipitation, &c., greatly diminish the transparency of air. Wild gives the following numbers as representing the transparency coefficient of 1 metre of air:—

Dry air (free from dust)	0·99718
Air of a room (dry, but containing dust)	0·99520
Air free from dust, but saturated with aqueous vapour	0·99328

The refractive indices of dry air at standard temperature and pressure for the Fraunhofer lines A, B, C, D, E, F, G, H, are, according to Kettler (Pogg. Ann. 124–401), as follows:—

nA=1·00029286	nE=1·00029584
nB=1·00029345	nF=1·00029685
nC=1·00029383	nG=1·00029873
nD=1·00029470	nH=1·00030026

The emission spectrum of air has been mapped by Huggins (Phil. Trans. 154, 139) and Angström (Pogg. Ann. 94, 141), and the spectrum of lightning by Kundt (Pogg. Ann. 135, 315), who has shown that forked lightning gives a line spectrum, whereas sheet lightning gives a band spectrum. The absorption spectrum of air was first mapped by Brewster and Gladstone, and has been further examined by Janssen, Cornu, and Chappuis (Compt. rend. 91, 988).

Air, owing to the oxygen it contains, is a magnetic substance. The diurnal variation in magnetic declination has been alleged to be due to the varying magnetic potential of the oxygen owing to alterations in temperature.

Air is a mixture of nitrogen, oxygen, aqueous vapour, argon, carbon dioxide, with minute quantities of ozone, hydrogen peroxide, ammonia, nitrous and nitric acids, hydrocarbons, helium, neon, krypton, xenon, hydrogen, &c. That the air is not a chemical compound of its component gases is proved by the facts: (1) that these gases are not present in any constant ratio; (2) that air can be made by simply mixing its constituents in the proportion indicated by the analysis of air, without contraction or any thermal disturbance resulting; (3) that on treating air with water and expelling the dissolved air by boiling, the proportion of the oxygen to the nitrogen is found to be increased, and in amount corresponding with the law of partial pressures; (4) that the constituents of the air can be mechanically separated by processes of diffusion; and (5) that the refractive power of the air is equal to the mean of the refractive powers of its constituents, whereas in compound gases the refractive power is either greater or less than the refractive power of the elements in a state of mixture.

The amount of oxygen in air may be ascertained by measuring the diminution in volume which a known bulk experiences when in contact with some substance capable of absorbing or combining with oxygen gas. Among the substances which may be conveniently used for this purpose are:

1. *Phosphorus.* A fragment of phosphorus on the end of a platinum or copper wire is exposed to a measured volume of air standing over water or mercury until no further decrease of volume is observed (Berthollet). Lindemann (Zeitsch. anal. Chem. 1879, 18, 158) employs thin sticks of phosphorus for the same purpose in the Orsat apparatus (*v.* GAS ANALYSIS). At a temperature below 7° the oxidation of the phosphorus ceases.

2. *Pyrogallol in Alkaline solution.* Chevreul, in 1820, first suggested the use of this reagent. The absorption is apt to be accompanied by the formation of notable quantities of carbon monoxide if the amount of oxygen is large or the alkaline solution very concentrated. According to Hempel (Ber. 20, 1865), the best proportions are 5 grams pyrogallol dissolved in 15 c.c.

water mixed with 120 grams caustic potash dissolved in 80 cm. of water. Practically, no carbon monoxide is formed with this solution. The absorption is very rapid (Hempel, Ber. 18, 267 and 1800).

3. *Metallic Copper.* A spiral of copper wire is heated to redness in dry air free from carbonic acid and of known pressure until the whole of the oxygen has combined with the metal to form cupric oxide. The pressure of the residual gas is then determined, whereby the amount of nitrogen is ascertained, and hence the amount of oxygen. An apparatus on this principle was suggested by Jolly (W. N. S. 6538); it is seen in Fig. 1.

The glass vessel A, of about 100 c.c. capacity, is exhausted by the mercurial pump, and is replenished with the air under investigation. This is then cooled to 0° by surrounding A

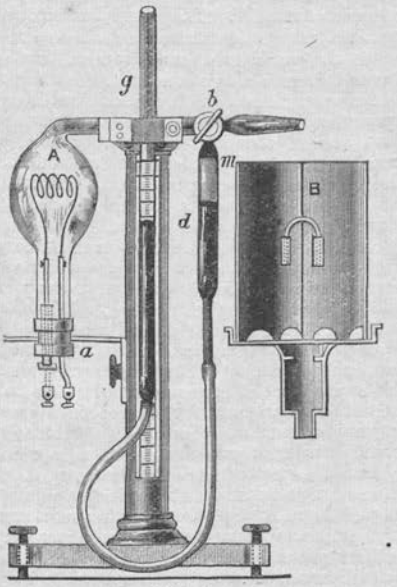


FIG. 1.

with the metallic cylinder B, which is filled with melting ice. The tension of the confined air is measured by the height of mercury in the glass tubes *g* and *d*, which are connected together by caoutchouc tubing. The tube *g* is movable in the clamp *f*, the position of *d* being fixed with reference to A. By turning the three-way stop-cock *b*, A and *d* may be alone brought into connection, or both may be made to connect with the outer atmosphere. The cock is now so turned that A and *d* are alone in connection; the tube *g* is now raised until the level of the mercury in *d* just touches the point *m*, when the tension of the air is read off on the graduated scale behind *g*. The copper spiral in A is next heated to redness by an electric current, whereby the heated metal rapidly combines with the oxygen. The cylinder B is once more placed round A, the residual nitrogen cooled down to 0° by means of melting ice, and its tension measured by adjusting the level of the mercury to *m*, and reading off the height of the mercury in *g*. If, for example, the pressure before abstracting the oxygen was 702·56 mm., and after the abstraction was 555·70 mm., then 1 volume of the air would be reduced to $=\frac{555{\cdot}70}{702{\cdot}56}=0{\cdot}79096$ vol., or, expressed centesimally, the composition of the air would be:

Nitrogen (argon, &c.) . .	79·096
Oxygen	20·904
	100·000

Kreusler has shown that unless the air be carefully dried before being heated with the copper spiral, the proportion of oxygen will be apparently too low.

Dumas and Boussingault (Ann. Chim. Phys. [3] 3257), as far back as 1841, made use of the fact that heated metallic copper combines with oxygen, in order to determine the gravimetric composition of air. Air deprived of moisture and carbonic acid was passed through a weighed tube containing metallic copper heated to redness, whereby all the oxygen was absorbed, the nitrogen being collected in a vacuous glass globe also previously weighed. At the conclusion of the experiment the tube containing the metallic copper was again weighed; the increase in its weight gave the amount of absorbed oxygen, together with the weight of the nitrogen which it also contained. The nitrogen was then removed by the air pump and the tube again weighed; the difference between the first and third weighings of the tube containing the copper gave the weight of absorbed oxygen, and the weight of nitrogen was obtained by adding the difference between the second and third weighings of the tube to the increase in the weight of the glass globe. As the mean of a large number of experiments made by this method, the precentage composition by weight of air free from water and carbonic acid was found to be

Oxygen	23·00
Nitrogen (with argon, &c.) .	77·00
	100·00

Leduc has shown that this proportion of oxygen is too low, as an average; the amount is about 23·2 p.c. by weight as calculated from the known density of air and of its constituent gases (Compt. rend. 1896, 12, 1805; 1898, 126, 413).

4. *Explosion with hydrogen.* A measured volume of air is mixed with a known volume of hydrogen in excess, and the mixture is exploded by the electric spark, when the oxygen combines with the hydrogen in the proportion of 1 vol. of the former to 2 of the latter to form water. One-third of the contraction resulting from the explosion represents, therefore, the amount of oxygen in the air under examination. This method, first suggested by Volta, was perfected by Bunsen. Modifications of the method have been made by Regnault and Reiset, Williamson and Russell, Frankland and Ward, and others. These methods are extremely accurate, and have afforded us all the exact knowledge we have respecting the variations in the amount of oxygen in atmospheric air. Thus Bunsen, in a series of analyses made in the winter of 1846, found that the percentage amount varied from 20·97 to 20·84. Regnault made a large number of analyses of air collected from all parts of the

world. In 100 analyses of air collected in Paris the minimum amount of oxygen was 20·913, the maximum 20·999. Air collected in various parts of Europe, from above the Atlantic Ocean, from the summits of the Andes and from the South Polar Sea, contained an amount of oxygen varying from 20·86 to 21 p.c. Many hundreds of analyses were made by Angus Smith, of air collected in various towns in England and Scotland, and also of air collected in the country. The oxygen in London air varied from 20·857 to 20·95, less oxygen as a rule being found in the air of streets than in that of the parks and open spaces. A series of 30 analyses of Glasgow air showed variations from 20·887 in the closer parts to 20·929 in the more open spaces. Even wider extremes were found by Leeds in the air of New York, viz. from 20·821 to 21·029 p.c. According to E. W. Morley, the diminished proportion of oxygen may be caused by the down-rush of air from the higher regions of the atmosphere, which probably contain a less relative amount of oxygen. Regnault's experiments afford some evidence for the belief that the air of the tropics contains slightly less oxygen than that in northern latitudes (*v.* also Jolly, W. N. F. 61, 520). A similar conclusion has been drawn by Hempel (Ber. 20, 1864) from the analysis of a large number of analyses of air collected simultaneously at Tromsö, Dresden, and Paris. The mean results were:

	Oxygen
Tromsö	20·92
Dresden	20·90
Paris	20·89

From the results of 203 analyses of air collected at five different spots and analysed by three independent methods, it follows that the most probable mean percentage amount of oxygen is 20·93. Numerous determinations by Pettersson and Högland of the air of Stockholm during October, November, and December, 1889, gave O=20·94 (Ber. 22, 3324; Hempel, Ber. 20, 1864; Kreusler, Ber. 20, 991).

Ozone is always present in minute quantity in normal air. Air over marshes contains little or no ozone. No ozone can be detected in the air of large towns or in inhabited houses. Atmospheric ozone is probably formed by the action of electricity on air and on the water contained in it, and by the evaporation of water. No accurate quantitative method is known for the estimation of ozone; all the information we at present possess has been obtained by the use of so-called ozone papers. Of these the best known is Schönbein's, which is based on the fact that ozone liberates iodine from potassium iodide, and thereby renders starch blue. To prepare them, unsized paper is immersed in a solution of 15 parts starch and 1 part potassium iodide in 200 parts of water and dried in the dark. To make a determination of ozone the paper is freely exposed to the air for some hours and moistened with water, and the depth of tint produced compared with a standard scale of colour. The method has no pretensions to scientific accuracy. Houzeau (Ann. Chim. Phys. 4, 27, 5) determines the relative amount of ozone by exposing red litmus paper previously dipped in 1 p.c. sol. of potassium iodide and dried, to the action of the air. The ozone liberates iodine and the free alkali turns the paper blue. Thallium salts are turned brown by the action of ozone, and hence papers soaked in solution of these salts have been used for the recognition of ozone. Paper soaked in a very dilute solution of neutral gold chloride is turned a deep violet colour by ozone (Böttger, Chim. Zentr. 1880, 719).

Attempts have been made to estimate ozone by aspirating large volumes of air through dilute solutions of hydriodic acid and determining the amount of the liberated iodine by iodometric analysis. Also by leading the air through a mixed solution of potassium arsenite and potassium iodide, whereby the liberated iodine converts the arsenite to arsenate. The liquid through which the air had passed was then mixed with a few drops of ammonium carbonate solution and starch paste, and a standard solution of iodine (1 : 1000) added until the blue colour was permanent. A precisely similar experiment was made on equal amounts of distilled water, iodine, arsenite, &c., used, and from the difference in the amount of iodine solution needed the amount of oxidised arsenite and hence the quantity of ozone was determined.

It appears that the amount of ozone varies with the seasons: it is greatest in winter, becomes gradually less during spring and autumn, and is least in summer. Ozone is more frequently observed on rainy days than in fine weather; thunderstorms, gales, and hurricanes are frequently accompanied by relatively strong manifestations of it (*cf.* Thierry, Compt. rend. 1897, 124, 460).

It is highly probable that many so-called ozone manifestations are due to *hydrogen peroxide*, the existence of which in the air was first demonstrated by Meissner in 1863. Unfortunately, there is no ready mode of discriminating between ozone and hydrogen peroxide. It is probable that the amount of hydrogen peroxide in the air is as a rule greater than that of ozone. Schöne found from observations made at Moscow, that it was invariably present in rain, dew, and snow, and was less in winter than in summer; and more in southerly winds than in those from the north. The amounts in all cases were, however, very minute, the maximum being 1·4 c.c., and the mean 0·38 c.c. hydrogen peroxide vapour in 1000 c.c. air.

The quantity of *aqueous vapour* in the air varies with the temperature: thus 1 cm. of air when saturated with water contains:

At −10°	2·284 grams	At +20°	17·157 grams
0°	4·871 „	25°	22·843 „
+ 5°	6·795 „	30°	30·095 „
10°	9·362 „	35°	39·252 „
15°	12·746 „		

The most accurate method of determining the amount of aqueous vapour in the air consists in aspirating a given volume of the air through weighed tubes filled with some hygroscopic substance, such as phosphoric oxide or pumice soaked in oil of vitriol and reweighing the tubes, when the increase of weight gives the quantity of moisture present.

Usually, however, the humidity of the air is estimated by means of hygrometers, the best-known form of which is the psychrometer or wet-and-dry-bulb thermometer of August. The *absolute humidity* of the air is the weight of aqueous vapour contained in 1 c.m. The *relative*

humidity denotes the relation between the weight actually present and that which could be theoretically present if the air were saturated; it is usually expressed in per cent. of the maximum humidity. The air is seldom absolutely saturated with aqueous vapour, although in our moist climate saturation is occasionally very nearly attained. With us the most humid month is December, and the driest is July.

The presence of *carbonic acid* in the atmosphere was first indicated by Black in 1752. The quantity in normal air is about 0·03 p.c.; in that of large towns it is slightly greater. Angus Smith gives the following summary of results obtained in London in 1864 and 1869 (Air and Rain, 53–58):—

Over River Thames .	8 expts.	0·0343 p.c.
In the Park . .	5 „	0·0301 „
In the streets . .	10 „	0·0380 „

Any circumstance which interferes with the ready diffusion of the products of respiration and of the combustion of fuel will tend to increase the relative amount of carbonic acid in the air of a town: hence during fogs the amount may be as great as 0·1 p.c.

The amount of carbonic acid in the air of the country at night is usually greater than in the day, as the following comparison shows:—

Air in the day-time.

Observer	Year	Place	Amount
Fr. Schulze .	1861–71	Rostock .	0·0292 p.c.
T. Reiset . .	1873–80	Ecorcheboeuf	0·0290 „
G. F. Armstrong	1879	Grasmere .	0·0296 „
Müntz & Aubin .	1881	Vincennes .	0·0284 „
A. Levy . .	1877–83	Montsouris .	0·0299 „
Petermann .	1892	Gemploux .	0·0299 „
Brown & Escombe	1898–1901	Kew . .	0·0294 „

Air in the night-time.

T. Reiset . .	1873–80	Ecorcheboeuf	0·0304 p.c.
G. F. Armstrong	1879	Grasmere .	0·0330 „

These differences are mainly due to the exhalation of carbonic acid from plants at night, and, to a smaller extent, to the absence of wind and of any decomposition of the gas by the action of sunlight. Over the sea this diurnal variation is not perceived, as the following results indicate:—

Carbonic acid in sea air.

T. E. Thorpe	Irish Channel and Atlantic Ocean	1865–6	Day .	0·0301 p.c.
			Night	0·0299 „
			Mean	0·0300

Comparatively few observations of the amount of carbonic acid in other parts of the earth than Europe have been made. The following may be cited:—

Carbonic acid in the air of tropical countries.

T. E. Thorpe .	S. America .	1866		0·0328 p.c.
Müntz & Aubin .	S. and Central America .	1882		0·0278 „
			Mean	0·0303

The pressure exerted by the carbonic acid in air is so small that its amount is not perceptibly diminished by rain. The amount also is not sensibly altered in the higher regions of the atmosphere.

Of the several methods which have been proposed for the estimation of atmospheric carbonic acid, the most generally convenient is that of Pettenkofer. It consists in exposing a known volume (say 50 c.c.) of dilute baryta water of known strength to a measured quantity of air (4–6 litres) contained in a well-closed flask. In about 5 or 6 hours the absorption of the carbonic acid will be complete, provided that the sides of the flask have been moistened from time to time by the baryta solution. The baryta solution is then decanted and allowed to stand in a small stoppered bottle until the barium carbonate has settled, when aliquot portions (say 20 c.c.) of the clear solution are withdrawn and the amount of the baryta still in solution determined by titration with a standard solution of sulphuric or hydrochloric acid, of which 1 c.c. = 1 mgm. CO_2, phenolthalein being used as indicator (*v.* ACIDIMETRY). The difference in the volume of acid needed for the neutralisation of the baryta before and after exposure to the confined volume of air gives the number of milligrams of carbonic acid contained in the air. Blochmann (Annalen, 237, 72) has described a modification of the apparatus which allows of the titration being effected without exposure to the air of the laboratory.

(For other methods, *v.* Haldane and Pembrey, Roy. Soc. Proc. 1889; Cl. Winkler, Chem. Unter. der Industriegase, Freiberg, 1877; Reiset, Chem. Soc. Trans. 90, 1144; Müntz and Aubin, Compt. rend. 92, 247.)

(For Angus Smith's minimetric method, *v.* Air and Rain; compare Lunge, Dingl. poly. J. 231, 331.)

(On the influence of the sea upon the amount of atmospheric carbonic acid, *v.* Levy, Ann. Chim. Phys. [3] 34, 5; Thorpe, Chem. Soc. Trans. 1867; Schloesing, Compt. rend. 93, 1410; Lawes, Phil Mag. [5] 11, 206.)

Minute quantities of ammonia and nitrous and nitric acids are also present in the air. Although many of the published observations are probably inaccurate owing to the imperfection of the methods employed, it appears to be proved that the amount of ammonia, which exists mainly as carbonate, is subject to very great variations. By aspirating from 10 to 20 litres of air through Nessler's solution (an alkaline solution of potassium-mercury iodide) and comparing the depth of colour with that produced by a standard solution of an ammonium salt, H. T. Brown (Roy. Soc. Proc. 18, 286) found that the air of Burton-on-Trent during September, October, and November, 1869, taken 2 metres from the ground, contained from 0·4059 to 0·8732 part $(NH_4)_2CO_3$ in 100,000 parts of air, whereas that of the country taken during December and February contained from 0·3102 to 0·6085 part. The direction of the wind had apparently no influence on the amount; heavy rain seemed to diminish it, but the air was restored to its normal condition in a few hours. Truchot found from 0·93 to 2·79 mgm. per cubic metre in the air of Auvergne, the minimum being found in clear weather and the maximum during fogs (Compt. rend. 77, 1059). Müntz and Aubin, from observations on rain water,

found that the upper strata of air contain much less ammonia than air near the ground. Levy (Compt. rend. 91, 94) found that the rain water and snow of Paris contain in mean 1·17 mgm. of ammoniacal nitrogen per litre of water. The amount of ammonia in this meteoric water is least in winter and greatest during the warmer periods of the year. Gilbert and Lawes found that 1,000,000 pts. of rain water collected in the country contained 0·927 to 1·142 pts. of ammonia. Rain water collected in towns always contains large quantities of ammonia. Thus Angus Smith found that rain water collected in the sparsely populated districts in Scotland contained 0·53 pt. per million, whereas the rain water of London contained 3·45, that of Liverpool 5·38, that of Manchester 6·47, and that of Glasgow 9·1 per million. The increased amount in the towns is doubtless due to the influence of animal life and to the constant presence in greater proportion than in the country of readily decomposable nitrogenous organic matter in the air (*cf.* Heinrich, Chem. Soc. Abst. 1898, ii. 114).

The quantities of nitrous and nitric acids in the air are even smaller than that of ammonia. Angus Smith (Air and Rain, 287) has given the following results showing the amount contained in a million pts. of rain water :—

Scotland, inland country places .	0·305
Ireland „ „ „ .	0·370
Scotland, country places . .	0·424
„ towns . . .	1·164
England, inland country places .	0·749
„ towns . . .	0·863

Occasionally, and more especially in the air of towns, minute quantities of hydrocarbons, sulphuretted hydrogen, carbonic oxide, sulphurous acid, common salt, alkaline sulphates, are met with. Boracic acid and sal ammoniac have been observed in air in the neighbourhood of active volcanos.

The percentage amount by volume of the inert gases in the air may be stated as follows :—

Argon	0·93000 p.c.
Krypton . . .	0·00995 „
Xenon	0·00114 „
Neon	0·00123 „
Helium . . .	0·00040 „

(Moissan, Compt. rend. 137, 600; Ramsay, Roy Soc. Proc. 1908, 80 A, 599.)

Organic matter in greater or less quantity is always present in the air. Much of this is nitrogenous, and apparently readily susceptible to putrefaction, giving rise to products which are alternately transformed into ammonia, nitrous and nitric acids. This form of organic matter reduces silver nitrate and potassium permanganate solutions. A portion of the organic matter consists of micro-organisms which are rapidly deposited in the absence of strong aërial currents. Hesse quantitatively estimates the relative proportions of micro-organisms contained in air by aspirating a given volume of the air through glass tubes coated internally with gelatine peptone, which is then kept at a temperature of about 25° for some days, when the various monad bacilli and micrococci which are arrested and which are capable of growing in the gelatine peptone are recognised by the colonies which they form. By means of this method Percy F. Frankland has made a number of estimations of the micro-organisms contained in the air of towns and in the country and in inhabited buildings. By simultaneously exposing small circular glass dishes partially filled with the nutrient gelatine to the action of the air, a rough estimate was obtained not only of the number of micro-organisms in a given volume of the air, but also of the number which fell during a given time on a definite horizontal area. As the mean of a series of observations made on the roof of the South Kensington Museum between January and June, 1886, it was found that there were 35 organisms in 10 litres of air, whilst 279 was the average number which fell on 1 sq. ft. in 1 minute. Similar experiments made near Reigate and in the vicinity of Norwich showed an average of 14 organisms in 10 litres of air, while 79 fell per sq. ft. per minute. Experiments made in Kensington Gardens, Hyde Park, and on Primrose Hill, gave an average of 24 organisms in 10 litres, and a deposition of 85 per sq. ft. per minute. At St. Paul's Cathedral, 56 organisms were found at the base, 29 in the Stone Gallery, and 11 in the Golden Gallery, in 10 litres of air. At Norwich Cathedral, 18 at the base, 9 at a height of 180 ft. and 7 at 300 ft. In inhabited buildings great variations were observed; as a rule, the number of micro-organisms was less than was found in the open air when the air of the room was undisturbed, but rose rapidly when the air was set in motion by draughts or by the presence of many people (P. F. Frankland, Roy. Soc. Proc. 40, 509).

Experiments made at the Montsouris Observatory have shown that far fewer organisms are present in the air during winter than during spring and summer. The number also seems to be greatly increased after rain. Whilst in the warm months the number of spores in 1 litre of air was 28, after heavy rain it rose to 95 and 120.

Atmospheric dust is made up of both inorganic and organic matter. Tissandier found that 1 c.m of the air of Paris contained on the average 7·5 mgms. of dust; after a period of dry weather (8 days), 23·0 mgms., and after heavy rain, only 6·0 mgms. It consisted of from 27 to 34 p.c. volatile matter, and from 66 to 75 p.c. mineral matter, viz. sulphates and chlorides of the alkalis and alkaline earths, oxides of iron, earthy carbonates and phosphates, &c. (*cf.* J. Aitken, Trans. Roy. Soc. Edin. 35, 37, 39).

Radioactive Constituents of the Atmosphere.

A charged electroscope slowly loses its charge in air, and it has been shown that this is not due to moisture, but that, on the contrary, the leakage is greater in dry than in wet weather. The conductivity of air is lessened by passage through a metal tube or by the presence of a weak electric field. These facts indicate that the conductivity of air is due to the presence of charged ions (Townsend, Proc. Roy. Soc. 1899, 65, 192; Geitel, Naturw. Rundsch. 21, 221). The rate of leakage of electricity from a charged conductor in dust-free air is the same for positive and negative charges, but varies with the pressure. The loss of charge per second corresponds to the production of about 20 ions

ATOMIC WEIGHTS AND SYMBOLS OF THE ELEMENTS (O=16).

Aluminium	Al	27·1	
Antimony	Sb	120·2	
Argon	A	39·88	
Arsenic	As	74·96	
Barium	Ba	137·37	
Bismuth	Bi	208·0	
Boron	B	11·0	
Bromine	Br	79·92	
Cadmium	Cd	112·40	
Cæsium	Cs	132·81	
Calcium	Ca	40·07	
Carbon	C	12·005	
Cerium	Ce	140·25	
Chlorine	Cl	35·46	
Chromium	Cr	52·0	
Cobalt	Co	58·97	
Columbium	Cb	93·1	
Copper	Cu	63·57	
Dysprosium	Dy	162·5	
Erbium	Er	167·7	
Europium	Eu	152·0	
Fluorine	F	19·0	
Gadolinium	Gd	157·3	
Gallium	Ga	69·9	
Germanium	Ge	72·5	
Glucinum	Gl	9·1	
Gold	Au	197·2	
Helium	He	4·00	
Holmium	Ho	163·5	
Hydrogen	H	1·008	
Indium	In	114·8	
Iodine	I	126·92	
Iridium	Ir	193·1	
Iron	Fe	55·84	
Krypton	Kr	82·92	
Lanthanum	La	139·0	
Lead	Pb	207·20	
Lithium	Li	6·94	
Lutecium	Lu	175·0	
Magnesium	Mg	24·32	
Manganese	Mn	54·93	
Mercury	Hg	200·6	
Molybdenum	Mo	96·0	
Neodymium	Nd	144·3	
Neon	Ne	20·2	
Nickel	Ni	58·68	
Niton (radium emanation)	Nt	222·4	
Nitrogen	N	14·01	
Osmium	Os	190·9	
Oxygen	O	16·00	
Palladium	Pd	106·7	
Phosphorus	P	31·04	
Platinum	Pt	195·2	
Potassium	K	39·10	
Praseodymium	Pr	140·9	
Radium	Ra	226·0	
Rhodium	Rh	102·9	
Rubidium	Rb	85·45	
Ruthenium	Ru	101·7	
Samarium	Sa	150·4	
Scandium	Sc	44·1	
Selenium	Se	79·2	
Silicon	Si	28·3	
Silver	Ag	107·88	
Sodium	Na	23·00	
Strontium	Sr	87·63	
Sulphur	S	32·06	
Tantalum	Ta	181·5	
Tellurium	Te	127·5	
Terbium	Tb	159·2	
Thallium	Tl	204·0	
Thorium	Th	232·4	
Thulium	Tm	168·5	
Tin	Sn	118·7	
Titanium	Ti	48·1	
Tungsten	W	184·0	
Uranium	U	238·2	
Vanadium	V	51·0	
Xenon	Xe	130·2	
Ytterbium (Neoytterbium)	Yb	173·5	
Yttrium	Yt	88·7	
Zinc	Zn	65·37	
Zirconium	Zr	90·6	

of either sign in each cubic centimetre of air (Wilson, Proc. Roy. Soc. 68, 151).

Elster and Geitel have shown (Wied. Ann. [2] 39, 321) that ions are produced during the formation of ozone by contact of air with flames or by the slow oxidation of phosphorus, &c., but the mere presence of ozone does not impart conductivity to air (Jorissen and Ringer, Ber. 1906, 39, 2090). Langevin (Compt. rend. 1905, 140, 232) states that in air, in addition to ordinary ions carrying charges equal to that of a hydrogen ion in solution, there exist other ions having a much smaller mobility, but carrying charges fifty times as great.

Nordmann has described (Compt. rend. 140, 430) an apparatus for continuously recording the state of ionisation of the air. Air is caused to circulate between the plates of a cylindrical condenser, and the charge given up by the ions is removed by dropping water. The condenser is connected with an electroscope, the deviations of which are recorded photographically, and are proportional to the number of ions present in unit volume of air. Another apparatus for the same purpose is that of Langevin and Moulin (Compt. rend. 140, 305).

No satisfactory explanation of the ionisation of air was found until Elster and Geitel showed (Physikal. Zeitsch. 1901, 76, 590) that a negatively charged wire suspended in the open air became coated with radioactive matter, the presence of which could be proved by its action upon a charged electroscope, although the quantity present was altogether too small to respond to any chemical test. Rutherford and Allan confirmed this observation, and measured the rate of decay of the deposit (Phil. Mag. 1902, vi. 4, 704). Later, Allan showed that the radioactive matter could be removed from the wire by rubbing it with a piece of felt or by solution in ammonia, and that the ashes of the felt or the residue from the evaporation of the solution showed radioactivity having a period of decay equal to that of the deposit on the wire (Phil. Mag. 1904, vi. 7, 140).

These phenomena are due to the presence in the atmosphere of the gaseous emanations of radioactive elements, probably those of radium and thorium (Bumstead, Amer. J. Sci. 1904, 18, 1). The amount of active matter is not constant, but increases with increased circulation of the air, and is therefore probably due to the presence of radium in the soil (Simpson, Phil. Trans. 1905, A, 205, 61). Balloon observations made by Flemming (Zeitsch. physikal. Chem. 1908, 9, 801) show that radium emanation is present even at a height of 3000 metres. Thorium emanation exists principally in air taken from the soil or the lower layers of the atmosphere (Gockel and Wulf, Physikal. Zeitsch. 1908, 9, 907). That it is not widely disseminated in the air is probably due to its rapid rate of decay (Blanc, Physikal. Zeitsch. 1908, 9, 294). The experiments of Dadourian (Physikal. Zeitsch. 1908, 9, 333) and of Wilson (Phil. Mag. 1909, 17, 321) indicate that air normally contains about 3700 times as much radium emanation as thorium emanation.

By passing air through a copper spiral cooled in liquid air, the emanations are condensed, and may then be volatilised into an electroscope and the amount estimated by their effect in ionising the contained air. Ashman (Amer. J. Sci. 1908, 26, 119) has thus found in Chicago air an amount of emanation per cubic metre equal to that which would be in equilibrium with about $1{\cdot}0\times10^{-10}$ gram of radium. By absorbing the emanations in charcoal and then volatilising them into an electroscope, Eve has obtained results of the same order—$0{\cdot}8\times10^{-10}$ gram for the radium equivalent of the emanation in the air of Montreal (Phil. Mag. 1907, 14, 724), and has shown by numerous observations that the value is not affected by temperature, but that a deep cyclone with rain causes an increase, whilst anti-cyclonic conditions cause a decrease in the amount of emanation (Phil. Mag. 1908, 16, 622). These results have been confirmed by Satterly (Phil. Mag. 16, 584).

All investigators are agreed that these emanations are the chief cause of the ionisation of air, but Wilson, by experiments on the effect of pressure on 'natural' ionisation of air enclosed in a metal cylinder, has shown (Phil. Mag. 1909, 17, 216) that it is partly due to some penetrating radiation the source of which is not in the soil (Pacini, Atti R. Acad. Lincei, 1909, 18, 123). Both Pacini and Wulf (Physikal. Zeitsch. 1909, 10, 152) have detected a double diurnal periodicity in the state of ionisation of the air.

(*See* also Harvey (Physikal. Zeitsch. 1909, 10, 46) and Runge (Chem. Soc. Abstr. 1908, ii. 80).)

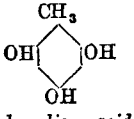
ATOXYL. Trade name for the mono-sodium salt of *p*-aminophenylarsinic acid (Ehrlich and Bertheim). Forms a white crystalline tasteless, odourless powder. So named from its relatively low toxic action (*v.* ARSENIC, ORGANIC COMPOUNDS OF).

ATRAMENTUM STONE. (*Atramentumstein*, Ger.) A product of the partial oxidation of iron pyrites, consisting of a mixture of ferrous and ferric sulphates with free ferric oxide. Used in the manufacture of ink.

ATRANORIN $C_{19}H_{18}O_8$ is present in the lichens *Evernia vulpina, E. prunastri, E. furfuracea, Lecanora atra, L. sordida, Parmelia perlata, P. physodes, Physcia stellaris, Xanthoria parietina, Cladonia rangiformis*, and *Stereocaulan vesuvianum*. It forms colourless prisms; m.p. 195°–197° (Zopf), 187°–188° (Hesse); easily soluble in hot chloroform, soluble in alkalis with a yellow colour.

According to Paternò, by heating with water to 150°, atranorin gives *physciol* (methyl-phloroglucinol), and *atraric acid* (betorcinol carboxylic acid methyl ester), and these substances are also obtained when atranorin is heated with acetic acid in a sealed tube (Hesse).

Physciol forms colourless needles, m.p. 104°–105°, gives with ferric chloride a blue-green colouration, and possesses, according to Hesse, the constitution of a methylphloroglucinol



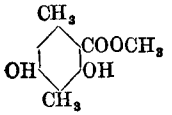
Betorcinol carboxylic acid methyl ether $C_{10}H_{12}O_4$, crystallises in leaflets, m.p. 140°–141°; and gives with calcium hypochlorite solution a blood-red colouration. Digested with boiling

hydriodic acid, it is converted into *β-orcin* (Stenhouse and Groves) $C_8H_{10}O_2$, according to the equation :

$$C_{10}H_{12}O_4+HI=CH_3I+CO_2+C_8H_{10}O_2.$$

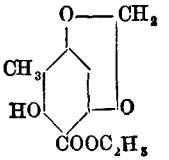
β-Orcin (*see* also *Barbatic acid*) is 1·4-dimethylresorcin.

The constitution assigned to betorcinol carboxylic acid methyl ether is :—



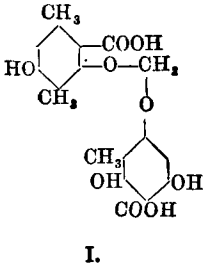
Heated with alcohol in a sealed tube, atranorin gives, according to Paternò, *Hæmatommic acid* and *Hæmatomminic acid*; but the researches of Hesse indicate that these compounds in reality consist of *hæmatommic acid methyl ether* and *betorcinol carboxylic acid methyl ether*.

Hæmatommic acid methyl ether $C_{10}H_{10}O_5$ forms colourless needles, m.p. 147°, soluble in alkaline solutions with a yellow colour. With ferric chloride it gives a purple-red or purple-brown colouration. The *ethyl ether*, $C_{11}H_{12}O_5$, gives colourless needles, melts at 111°–112° (Hesse); 113°–114° (Zopf). It is represented by the formula :—

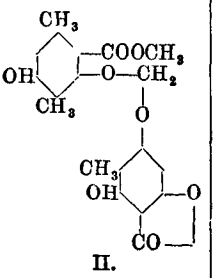


When a solution of atranorin in dilute acetic acid is gently evaporated, *atranorinic acid* (Hesse) is produced. This compound is also present in the *Cladonia rangiformis* (Hesse) when gathered in December, but is absent from this lichen in summer.

Atranorinic acid $C_{18}H_{18}O_9,H_2O$ forms colourless crystals, which are anhydrous at 100°, and then melt at 157°. With ferric chloride it gives a dark brownish-red colouration. Heated with hydriodic acid it gives *β-orcin*, or with alcohol yields carbon dioxide, *physciol* and *β-orcin*. The constitutions assigned to atranorinic acid (I.) and atranorin itself (II.) are as follows :—



I.



II.

References.—Paternò and Oglialaro (Gazz. chim. ital. 7, 289), Paternò (*ibid.* 10, 157 and 12, 257); Zopf (Annalen, 288, 38); Hesse (J. pr. Chem. 57, 280); Lüdecke (Annalen, 288, 42); Hesse (Annalen, 119, 365); Stenhouse and Groves (Annalen, 203, 302). A. G. P.

ATROLACTINIC ACID *v.* LACTIC ACID.

ATROPINE *v.* VEGETO-ALKALOIDS.

ATTAR OF ROSES *v.* OILS, ESSENTIAL.

AUCUBIN *v.* GLUCOSIDES.

AURAMINE. *Iminotetramethyldiparamino-diphenylmethane hydrochloride*, $C_{17}H_{21}N_3,HCl,H_2O$; $NMe_2{\cdot}C_6H_4C(NH){\cdot}C_6H_4{\cdot}NMe_2,HCl,H_2O$ (Graebe), or $Me_2N{\cdot}C_6H_4{\cdot}C(NH_2):C_6H_4:NMe_2Cl,H_2O$ (Stock; Dimroth and Zoeppritz). According to Stock (J. pr. Chem. 47, 401; Ber. 1900, 33, 318), and Dimroth and Zoeppritz (Ber. 1902, 35, 984), the base has the constitution assigned to it by Graebe (Ber. 1899, 32, 1678; 1902, 35, 2615), but the hydrochloride and the other salts have the quinonoid structure $Me_2N{\cdot}C_6H_4{\cdot}C(NH_2):C_6H_4:NMe_2Cl$, and are to be regarded as derivatives of triphenylmethane in which an amino- group has replaced one of the benzene residues.

Auramine, the first member of a series of yellow, orange-yellow, or brown dyes, is the hydrochloride of a colourless base obtained by the action of ammonia on tetramethyldiaminobenzophenone, and comes into the market either in the nearly pure form as *Auramine O*, or mixed with dextrin as *Auramine I.* and *II.* (Graebe, Ber. 20, 3264). Fehrmann (Ber. 20, 2847) proposed to restrict the name auramine to the colourless base, but such a change would inevitably lead to confusion; and Graebe (*l.c.*) has consequently adopted the name *auramine-base* for the base itself, using the term auramine in its usual signification.

Preparation.—(1) Auramine was originally prepared from tetramethyldiaminobenzophenone by dissolving it in some indifferent solvent such as chloroform, carbon disulphide, hydrocarbons, &c., treating it with half its weight of phosphorus trichloride or oxychloride, and adding excess of concentrated ammonia to the chlorinated compound thus obtained (B. A. S. F., D. R. P. 27789).

(2) Auramine can be prepared more economically by heating tetramethyldiaminobenzophenone with suitable ammonium salts, such as the chloride, acetate, tartrate, thiocyanate, &c., in the presence of zinc chloride at 200° (B. A. S. F., D. R. P. 29060). Acetamide may be employed instead of ammonium salts (B. A. S. F., D. R. P. 38433), or the dye may be obtained by heating aniline hydrochloride with zinc chloride and carbamide, phenylcarbamide, diphenylcarbamide, or carbanil (Ewer and Pick, D. R. P. 31936); but these alternative methods have no practical importance.

(3) At the present day, auramine is prepared by a method due to Sandmeyer (Eng. Pat. 12549, 1889; 16666, 1890) and Walker (J. Soc. Chem. Ind. 1901, 34), which consists in heating a mixture of tetramethyldiaminodiphenylmethane, sulphur, ammonium chloride, and sodium chloride in a current of dry ammonia. A modification of this method is described by J. Y. Johnson (B. A. S. F., D. R. P. 71320; Eng. Pat. 6249, March 23, 1893), in which the tetramethyldiaminodiphenylmethane is replaced by dimethyl-tetramethyldiaminodiphenylmethane obtained by condensing acetone and dimethylaniline (Ber. 1878, 12, 813). About 14 kilos. of dimethyl-tetramethyldiaminodiphenylmethane are mixed with 120 kilos. of salt, 6 kilos. of sulphur, and 7 kilos. of ammonium chloride, and a stream of ammonia gas is passed through the mixture for eight hours at 175°.

The mass is first washed with cold water to dissolve away the salt and ammonium chloride, it is then dissolved in water at 70°, filtered, and the dye salted out, pressed, and dried. Auramine is also prepared by heating dimethylaminobenzamide and dimethylaniline with zinc chloride at 160°–200° (D. R. P. 77329).

(4) Guyot (Compt. rend. 1907, 144, 1219; J. Soc. Chem. Ind. 1908, 679) has synthesised auramines by means of the oxalic esters. Tetraalkyldiaminodiphenylglycollic esters (J. Soc. Chem. Ind. 1907, 603) form neutral salts with acids, the indigo-blue aqueous solutions of which react with ammonia even when dilute to furnish tetraalkyldiaminodiphenylamino acetic esters, according to the equation:

$$(R_2N\cdot C_6H_4)_2CCl\cdot CO_2R'+2NH_3 = NH_4Cl+(R_2N\cdot C_6H_4)_2C(NH_2)CO_2R'.$$

These new compounds are *exo*-carboxylic derivatives of the leucauramines, and possess all the properties of the latter. They dissolve in glacial acetic acid with an intense blue colouration, and condense with aromatic tertiary amines to form triphenylmethane derivatives. Thus ethylhexamethyltriaminotriphenyl acetate is produced by heating an equimolecular mixture of dimethylaniline and ethyltetramethyldiaminodiphenylaminoacetate in glacial acetic acid on the water-bath for some minutes:

$$(Me_2N\cdot C_6H_4)_2C(CO_2Et)\cdot NH_2+C_6H_5\cdot NMe_2 = (Me_2N\cdot C_6H_4)_2C(CO_2Et)C_6H_4NMe_2+NH_3.$$

When a dilute alkaline solution of the aminoacetic ester is oxidised with dilute potassium ferricyanide solution in the cold, a quantitative yield of the corresponding auramine is produced.

Properties.—Auramine crystallises from water in yellow scales, which seem to consist of six-sided tables, and from alcohol in golden-yellow scales, melts at 267° (Graebe), carbonises at 265°–280° without previous fusion (Fehrmann), and is sparingly soluble in cold but readily soluble in hot water; the temperature of the aqueous solution, however, must not exceed 60°–70°, otherwise decomposition ensues, with the formation of ammonia and tetramethyldiaminobenzophenone. On treatment with mineral acids, the aqueous solution undergoes a similar decomposition either slowly in the cold or very rapidly on heating. Spectroscopically, auramine behaves like most yellow dyes; a hot concentrated aqueous solution, however, shows two bands, one in the red and one in the green, which become broader on dilution and finally coalesce, forming a bright broad band extending from the middle of the red to the commencement of the green (Graebe). On treatment in the cold with ammonia, auramine (crystallised from alcohol) is converted into the colourless base $C_{17}H_{21}N_3$, which melts at 136°, and is characterised by yielding with acids intensely yellow, and for the most part crystalline salts, which dissolve in water and alcohol without fluorescence. Alkaline reducing agents, such as sodium amalgam, slowly decolourise the alcoholic solution of auramine, forming *leucauramine* $C_{17}H_{23}N_3$, a colourless crystalline reduction compound melting at 135°, which dissolves in acetic acid with an intense blue colour owing to its decomposition into ammonia and tetramethyldiaminobenzhydrol.

Auramine dyes wool and silk direct, producing colours which are pure yellow and fairly fast to light and soap. Cotton, for which the dye is chiefly used, requires to be first mordanted with tannin and tartar emetic, and on this account auramine is useful for producing compound shades with other basic colouring matters, such as safranine, benzaldehyde-green, &c., which are fixed by the same mordant. (For further information *v.* Köchlin, Wagner's Jahr. 1884, 1139.)

Salts. *Auramine hydrochloride* $C_{17}H_{21}N_3$, HCl, is sparingly soluble in water, and has $\mu\infty$ 90·4 at 25°; the *palmitate* $C_{17}H_{21}N_3,C_{16}H_{32}O_2$, has m.p. 57°, the *stearate* has m.p. 68° (Gnehm, Röteli Zeit. Angew. Chem. 1898, 487); the *methyl sulphate* obtained by the action of dimethyl sulphate on auramine, has m.p. 225° (Zohlen, J. pr. Chem. 1902, 66, [20] 387).

Substituted Auramines. In addition to auramine, substituted auramines have also been prepared. **Auramine G**, obtained by treating a hot mixture of *sym*-dimethyldiamino-di-*o*-tolylmethane (from methyl *o*-toluidine and formaldehyde) sulphur, ammonium chloride and salt with dry ammonia gas (Gnehm and Wright, U.S. Pat. 488430), has m.p. 120°, the *picrate* has m.p. 234°, the *sulphate* m.p. 182°, the *oxalate* m.p. 210°. *Leucauramine G* has m.p. 208°.

Metaxylylauramine can be obtained by heating an intimate mixture of 10 kilos. of tetramethyldiaminobenzophenone and 23 kilos. of metaxylidine hydrochloride for about 4 hours at 200° in an enamelled vessel provided with a mechanical stirrer. Fusion takes place slowly, and the mass becomes reddish yellow in colour, assuming finally a greenish metallic lustre towards the close of the reaction, which is complete when a test specimen is almost entirely soluble in water. The cooled mass is extracted with hot water, and the dye precipitated in orange-yellow flocks by addition of sodium nitrate to the filtered solution.

Methylauramine MeN: $C(C_6H_4\cdot NMe_2)_2$, m.p. 133° (Zohlen, J. pr. Chem. 1902, 66, 387), the *hydrochloride* $C_{18}H_{24}N_3Cl$, has m.p. 225°, the *platinichloride* $(C_{18}H_{24}N_3Cl)_2PtCl_6$, m.p. 190°–200°, the *hydrobromide* $C_{18}H_{24}N_3Br$, m.p. 260°, the *hydriodide* $C_{18}H_{24}N_3I$, m.p. 259°, forms a series of unstable polyiodides: the *trichromate* $(C_{18}H_{24}N_3)_2Cr_3O_{10}$, m.p. 70°, the *thiocyanate* $C_{18}H_{24}N_3CNS$, m.p. 213°–214°, and the *picrate* $C_{18}H_{23}N_3,C_6H_3O_7N_3$, m.p. 225°.

Ethylauramine EtN: $C(C_6H_4\cdot NMe_2)_2$, from auramine ethyl iodide and zinc oxide (D. R. P. 136616), m.p. 130°–131°, dyes mordanted cotton a pure yellow.

Phenylauramine PhN: $C(C_6H_4\cdot NMe_2)_2$, prepared by heating tetramethyldiaminodiphenylmethane with aniline and sulphur at 200° (Feer, D. R. P. 53614); or by heating dimethylaminobenzanilide with dimethylaniline and phosphorus oxychloride (D. R. P. 44077); has m.p. 172°; the *hydriodide* $C_{23}H_{25}N_3,HI$, has m.p. 242°; the *methiodide* $C_{23}H_{25}N_3,MeI$, has m.p. 214°.

Paraminophenylauramine $NH_2\cdot C_6H_4N$: $C(C_6H_4\cdot NMe_2)_2$ (Finckh and Schwimmer, J. pr. Chem. 1894, 50, 401), has m.p. 221°–222°; the *hydrochloride*, m.p. 224°; the *picrate*, m.p. 185°–186° (corr.); the *diacetyl* derivative has m.p. 194°–195°; the *triacetyl* derivative has m.p. 257°–258°; *monobenzoyl* derivative has m.p. 117°; and the *dibenzoyl* derivative has m.p. 180°–181°;

paraphenylenediauramine $C_6H_4[N:C(C_6H_4\cdot NMe_2)_2]_2$, has m.p. 311°–312°.

Orthaminophenylauramine, m.p. 199°–200°, forms a *picrate*, m.p. 220°–221°, and a *benzoyl* derivative, m.p. 236°–237°; *orthophenylenediauramine* has m.p. 305°.

***p*-Tolylauramine**, obtained by heating tetramethyldiaminodiphenylmethane with *p*-toluidine and sulphur (D. R. P. 53614), or from dimethylaminobenzo-*p*-toluidine, dimethylaniline, and phosphorus oxychloride (D. R. P. 44077), has m.p. 178°. ***o*-Tolylauramine** similarly prepared to the *p*- compound has m.p. 173°–174°, **α-naphthylauramine** $(Me_2N\cdot C_6H_4)_2C:NC_{10}H_7$ (D. R. P. 44077), has m.p. 225°. **β-naphthylauramine** $(Me_2N\cdot C_6H_4)_2C:N\cdot C_{10}H_7$ (D. R. P. 44077), m.p. 179° – 180°. **Benzylauramine** $C_6H_5\cdot CH_2\cdot N:C(C_6H_4\cdot NMe_2)_2$ (D. R. P. 136616) from auramine benzylchloride and magnesia, has m.p. 116°. **Benzoylauramine** (Finckh and Schwimmer, J. pr. Chem. 1894, 50, 401) $NBz:C(C_6H_4\cdot NMe_2)_2$, has m.p. 179° (corr.).

Methylphenylauramine hydrochloride, *dephenylauramine*, and *pentamethyleneauramine* have been described by Stock (Ber. 1900, 33, 318; J. pr. Chem. 47, 401–413). The following compounds, closely related to the naphthylauramines, form the subject of a patent (D. R. P. 44077): *tetraethyldiaminodiphenylmethylene-α-naphthylamine* $(Et_2N\cdot C_6H_4)_2C:N\cdot C_{10}H_7$, m.p. 157°–158°; *dimethyldiethyldiaminodiphenylmethylene-α-naphthylamine* $(Me_2N\cdot C_6H_4)(Et_2N\cdot C_6H_4)C:N\cdot C_{10}H_7$, m.p. 177°–178°; *tetraethyldiaminodiphenylmethylene-β-naphthylamine* $(Et_2N\cdot C_6H_4)_2C:N\cdot C_{10}H_7$, m.p. 155°; *dimethyldiethyldiaminodiphenylmethylene-β-naphthylamine* $(Me_2N\cdot C_6H_4)(Et_2N\cdot C_6H_4)C:N\cdot C_{10}H_7$, m.p. 163°–164°.

The substituted auramines dye silk and wool, and also cotton after mordanting with tannin. The shades produced on cotton are, however, distinctly reddish or brownish-yellow compared with the pure yellow produced by auramine itself; for example, the auramines from orthotoluidine, metaxylidine and cumidine hydrochlorides dye cotton golden-yellow; those from aniline and paratoluidine dye orange-red, that from metaphenylenediamine dyes orange-brown, and those from α- and β-naphthylamine dye brownish-yellow shades (B. A. S. F., D. R. P. 29060; Fehrmann, Ber. 20, 2852).

AURANTIA (*Kaisergelb*) is the commercial name of the ammonium salt of hexanitrodiphenylamine.

Hexanitrodiphenylamine $NH[C_6H_2(NO_2)_3]_2$ is obtained by treating diphenylamine or methyldiphenylamine with nitric acid, and, after the first vigorous action has subsided, heating to complete the reaction. The product is then extracted with water to remove any resin or picric acid associated with it, and finally crystallised from acetic acid.

It forms bright-yellow prisms, melts at 238° with decomposition, but can be sublimed in yellow needles by careful heating, and is almost insoluble in water, more soluble in alcohol, and easily soluble in ether. It readily yields salts, and the *ammonium* salt (aurantia) crystallises in lustrous brown-red needles, although commercially it is obtained as a brick-red powder which dissolves in water and dyes silk and wool a beautiful orange colour (Gnehm, Ber. 7, 1399; 9, 1245; *cf.* Townsend, Ber. 7, 1249; Mertens, Ber. 11, 845). Aurantia is used chiefly as a dye for leather (W. J. 1877, 1002). Like hexanitrodiphenylamine, it is very explosive, but any danger may be avoided by moistening it with glycerol (W. J. 1876, 996). According to Gnehm (Ber. 9, 1246, 1557) and Bayer & Co. (W. J. 1877, 879), aurantia produces skin eruptions; Martius, however, contends that this effect is due to idiosyncrasy, and quotes the opinions of Salkowski and Ziureck in support of his statement (Ber. 9, 1247), and the question appears to have received a solution in this sense in Germany, since the ministerial order of November 8, 1877, prohibiting its manufacture, was cancelled in June, 1880.

AURIN and **ROSOLIC ACID.**

History.—Rosolic acid was first discovered and its tinctorial properties described by Runge (P. 31, 65), who obtained it from coal-tar oil by dissolving the residue from the distillation of phenol in alcohol, adding milk of lime, filtering off the brown precipitate of calcium brunolate and precipitating the red solution of calcium rosolate with acetic acid. Later, Tschelnitz (J. pr. Chem. 71, 416) and Müller (Chem. Soc. Trans. 11, 1) found that the yield was greater if the product after addition of the lime was heated in the air for some time, whilst Smith (J. 1857, 448) and Jourdin (J. 1861, 943) showed that crude phenol was converted into rosolic acid by heating it with soda and manganese dioxide or mercuric oxide. Kolbe and Schmitt (Annalen, 119, 169) and, simultaneously, Persoz (Fr. Pat. 54910, July 21, 1861) obtained it by heating phenol and oxalic acid with sulphuric acid, and this method was adopted for preparing the acid on the large scale by Wurtz (Schmidt, Dingl. poly. J. 166, 318) who termed it (yellow) corallin (known commercially as aurin in England), and by Guinon, Marnas and Bonnet (Dingl. poly. J. 167, 390), who converted it into pæonin or red corallin by digestion with aqueous ammonia at 150°. The reaction was further investigated by Fresenius (J. pr. Chem. [2] 5, 184), by Prud'homme (Zeitsch. angew. Chem. [2] 19, 359), and by Comaille (Compt. rend. 77, 678), the last of whom found that the proportion of oxalic acid used was too large. By diazotising rosaniline, Caro and Wanklyn (Chem. News, 14, 37; Proc. Roy. Soc. 15, 210) obtained rosolic acid $C_{20}H_{16}O_3$, which, however, was not identical with the product from phenol. Caro (Phil. Mag. [4] 32, 126), moreover, showed that the formation of rosolic acid from phenol is dependent on the presence of cresol or of some simple (methane) derivative of the fatty series of organic compounds (compare Guareschi, Ber. 5, 1055; Zulkowsky, Annalen, 194, 122). The nature and composition of the products obtained in Kolbe and Schmitt's reaction were not, however, accurately known until 1878, when the researches of Dale and Schorlemmer (Annalen, 166, 279; 196, 75), Caro and Graebe (Annalen, 179, 184; Ber. 11, 1116, 1348), E. and O. Fischer (Ber. 11, 473) and Zulkowsky (Annalen, 194, 122; 202, 179) established the fact that the action of oxidising agents on a mixture of phenol and cresol, or of oxalic acid on phenol, results in the formation of a mixture of red colouring matters (corallin) containing two well-characterised substances termed aurin $C_{19}H_{14}O_3$, and methylaurin $C_{20}H_{16}O_3$. Aurin is the lower homologue of Caro and

Wanklyn's rosolic acid, and is sometimes known as pararosolic acid, since it can be obtained by diazotising pararosaniline (E. and O. Fischer, Annalen, 194, 268).

Corallin. This name is applied to the red colouring matter obtained by heating phenol and oxalic acid with sulphuric acid. According to Zulkowsky (Annalen, 194, 122; 202, 134; Monatsh. 16, 363), a mixture of pure phenol (10 parts) and sulphuric acid of 66°B. (5 parts) is heated with anhydrous oxalic acid (6 parts) added in three equal quantities, at 120°–130° until the mass becomes viscid and the evolution of gas (a mixture of CO and CO_2 in equal volumes) slight. This stage is reached in about 24 hours, and the product is then poured into so much water that the further addition of water does not produce a precipitate. The corallin is thus separated from phenolsulphonic acid and unattacked phenol, and the yield by this process amounts to 60–70 p.c. Corallin has been shown to be a mixture of pseudo-rosolic acid or corallinphthalin (70 p.c.), to which it owes its resinous consistency, with aurin, methylaurin, and, according to Zulkowsky, with several other products, of which very little is known.

Properties.—It is a brittle resinous substance with a green metallic lustre, and yields a red powder. It has been employed as a dye for silk and wool (Schröder, Dingl. poly. J. 204, 397), and used for printing on cotton, silk, and wool. In printing with corallin, any acids with which it may come in contact during the process must be neutralised, otherwise a yellow instead of a turkey-red colour is the result. Kielmeyer recommends magnesia for this purpose (Wagner's Jahr. 1872, 709).

The following substances have been isolated from corallin :—

(1) **Aurin** (*pararosolic acid*) $C_{19}H_{14}O_3$ or $C(C_6H_4{\cdot}OH)_2 : C_6H_4 : O$. The formation of the aurin present in corallin has been attributed to the reaction :

$$3C_6H_6O+H_2C_2O_4=C_{19}H_{14}O_3+H_2CO_3+2H_2O$$

(D. and S. Annalen, 196, 79; compare, however, Zulkowsky, Annalen, 202, 184; E. and O. Fischer, Ber. 11, 201; Gukassianz, Ber. 11, 1179; Z. Ber. 11, 1431; Nencki and Schmid, J. pr. Chem. [2] 25, 273); Z. Monatsh. 5, 108; Staub and Smith, Ber. 17, 1740).

Preparation.—Aurin can be obtained by diazotising pararosaniline (E. and O. Fischer, *l.c.*; compare ROSOLIC ACID), but the process has no practical value. It can be obtained pure and in good yield (95 p.c. when zinc chloride is used) by heating phenol (14 parts) with carbon tetrachloride (8 parts) and zinc chloride (30 parts), or aluminium chloride (10 parts), or stannic or ferric chloride (20–30 parts) at 140°–160° in an autoclave during 4 hours with occasional stirring. The product, when cold, is purified by driving off unattacked phenol with steam, and removing soluble impurities by extraction with water (Heumann, D. R. P. 68976 of April 3, 1892, expired Aug. 1893; compare Friedel, Bull. Soc. chim. 50, 2). Elbs substitutes chloropicrin for carbon tetrachloride, heating the mixture for one to two days in a steam-bath, but does not state the yield (Ber. 16, 1275).

Reference has been made to Smith's and Jourdin's methods of oxidising crude phenol. Rudolph (Zeitsch. angew. Chem. 19, 384) heats paracresol (108 grams) and phenol (188 grams) dissolved in 32 p.c. caustic soda solution (400 grams) with sodium dichromate (300 grams) also dissolved in 32 p.c. caustic soda solution (250 grams) for some hours at 180° under pressure. The aurin is purified by conversion into the compound with sodium bisulphite.

Another process is that described by N. Caro (Ber. 25, 948), in which a mixture of dihydroxydiphenylmethane and phenol in mol. prop. is oxidised by a cold solution of sodium nitrite in concentrated sulphuric acid.

To obtain aurin from the commercial product, Dale and Schorlemmer (Annalen, 166, 280) treat a concentrated alcoholic solution of corallin with gaseous ammonia until crystals of the compound of aurin with ammonia cease to form; the precipitate is then heated with hydrochloric acid or acetic acid to remove ammonia, and the product repeatedly crystallised from alcohol. A second method, in which the commercial product is washed with cold alcohol and the residue repeatedly crystallised from alcohol, has also been described (D. and S. Annalen, 196, 77). A third method, due to Zulkowsky (Annalen, 202, 185), in which a solution of corallin in dilute soda ley is saturated with sulphur dioxide, and the resinous pseudo-rosolic acid or corallinphthalin precipitated by water, has been described. The separation of the aurin from the methylaurin, and leucorosolic acid left in solution, is effected by the aid of sulphur dioxide, with which aurin forms a crystalline compound. The process can be varied by dissolving corallin in a 1·25 p.c. solution of caustic soda, precipitating the clear solution by carbon dioxide, suspending the precipitate in water acidified with acetic acid, and washing it finally with water. The precipitate (1 part) is then dissolved in boiling alcohol (20 parts), and the aurin separated by adding to the solution one-fourth its volume of boiling water (Monatsh. 16, 363). The yield of aurin by any of these methods amounts to less than 10 p.c.

Properties.—Aurin crystallises in garnet-red rhombic forms, which appear rose-red by transmitted, and show a sky-blue lustre by reflected, light; it does not melt at 220°. In alcohol and acetic acid it dissolves, forming yellow-red, and in alkalis and ammonia carmine, solutions. Aurin combines with sulphur dioxide, forming the compound $H_2SO_3+(C_{19}H_{14}O_3)_2+4H_2O$, which crystallises in red cubes and cubic octahedra, showing a green metallic lustre (D. and S. Annalen, 166, 184; Z. Annalen, 202, 200); it also combines with alkaline bisulphites (D. and S.). Acetic anhydride converts it into two *triacetyl-* compounds, $C_{19}H_{13}O_4(C_2H_3O)_3$, m.p. 171°–172° and 146°–149°, from each of which aurin can be regenerated by hydrolysis (Herzig and Smoluchowski, Monatsh. 15, 73; Herzig, *ibid.* 17, 191). Bromine reacts with it in acetic acid solution to form *tetrabromaurin* $C_{19}H_{10}O_3Br_4$, which yields violet solutions with alkalis, and in acid solution is a dark-violet dye for silk and wool (D. and S. Annalen, 196, 81; compare Z. Monatsh. 3, 465; Ackermann, Ber. 17, 1624). With iodine in alkaline solution, or electrolytically with potassium iodide and an alkali, aurin yields a *triiodo-* derivative $C_{19}H_{11}O_3I_3$, for which some pharmaceutical value is claimed (Classen, D. R. P. 85929, of

May 27, 1894). *Tetranitroaurin* $C_{19}H_{10}O_3(NO_2)_4$, m.p. 140°, and several ethyl ethers have been prepared by Ackermann (*l.c.*; for *aurindimethyl ether* $C_{19}H_{12}O(OCH_3)_2$, *see* Herzig, Monatsh. 29, 653). When an alcoholic solution of aurin is saturated with ammonia, *aurin-ammonia* $C_{19}H_{14}O_3,(NH_3)_3$ is obtained; this crystallises in dark-red needles, and rapidly loses ammonia on exposure to air. If, however, aurin is heated with aqueous or alcoholic ammonia at 180°–200° for 20 hours, it yields paraleucaniline (D. and S. Annalen, 196, 75); and similar treatment with methylamine and aniline results in the formation of trimethyl- and triphenyl- rosaniline respectively. Reducing agents, and zinc-dust with acetic acid in particular, convert it into *paraleucaurin* $CH(C_6H_4{\cdot}OH)_3$, which crystallises from alcohol in colourless lustrous needles, does not melt at 130°, yields a *triacetyl-* derivative, melting at 138°–139°, and on oxidation with permanganate or ferricyanide of potassium, does not yield aurin, but an undetermined red product (Dale and Schorlemmer; Zulkowski; Caro and Graebe, *l.c.*).

The following hydroxyaurins have been prepared by Nencki (*J. pr. Chem.* [2] 25, 275): **cresolaurin** $C_{22}H_{20}O_3$; **resaurin** $C_{19}H_{14}O_4$; and **orcinolaurin**, $C_{22}H_{18}O_5$.

Other hydroxyaurins, and several aurincarboxylic acids have been made by N. Caro's process (*l.c.*, Ber. 25, 2671; J. R. Geigy and Co., D. R. P. 49970; E. P. 3333 of 1889). For example, **aurintricarboxylic acid** $C[C_6H_3(OH)CO_2H]_2:C_6H_3(OH):O$ can be obtained (*a*) by dissolving salicylic acid (2 parts) in concentrated sulphuric acid (15 parts) and methyl alcohol (4 parts), warming the solution to 60°–70° and adding solid sodium nitrite (1·5 parts); (*b*) by adding salicylic acid (2 parts) to a solution of sodium nitrite (1 part) in concentrated sulphuric acid (10 parts), and adding, with constant stirring, either formalin (0·5 part) or methylal (0·4 part). The product, a red powder, forms lakes with metallic oxides, of which that with chromic oxide is the most valuable, being fast to soap. The *ammonium* salt has found employment in calico-printing under the name chrome violet.

(2) **Methylaurin** $C_{20}H_{16}O_3$ crystallises in small brick-red crystals with a green metallic lustre. Bromine in acetic acid converts it into the compound $C_{20}H_{12}Br_4O_3,HBr+2H_2O$, which on boiling with water yields *tetrabromomethylaurin*; this dissolves in alcohol with a violet-red, and in alkalis with a magenta, colour. On reduction with zinc-dust and acetic acid, methylaurin yields the *leuco-* base $C_{20}H_{18}O_3$, crystallising in colourless rhombic needles (Z. *l.c.*; Monatsh. 3, 471).

(3) **Pseudorosolic acid** (*corallinphthalin* or *phenolcorallin*) $C_{20}H_{16}O_4$, is, together with other amorphous substances, the chief constituent of corallin. In colour it is red, with a green metallic lustre, and on oxidation with potassium permanganate yields corallinphthaleïn.

(4) Zulkowski (Monatsh. 16, 363) states that corallin, when prepared from pure phenol, contains, in addition to aurin, two colouring matters of the formulæ $C_{20}H_{16}O_4+H_2O$ and $C_{20}H_{16}O_5+H_2O$, of which the former is precipitated from solution in alkali by carbon dioxide, and the latter is not. Further, two isomeric substances, destitute of tinctorial properties, of the formula $C_{19}H_{14}O_4$, are contained in the filtrate, after precipitation with carbon dioxide, and recovered from it by neutralisation with hydrochloric acid; they are termed *α-* and *β-aurin oxides*. The nature of these four substances is unknown.

(5) In addition to the foregoing, **phenyl ortho-oxalate** $C_{14}H_{14}O_6$ sublimes during the preparation of aurin, and is found on the lids of the aurin pots in the form of colourless needles, melting at 128°. It plays no part, however, in the formation of aurin, but is produced by the action of phenol vapour on anhydrous oxalic acid (Claparède and Smith, Chem. Soc. Trans. 1883, 358; Staub and Smith, Ber. 17, 1740).

Pæonin (*red corallin* or *aurin R.*) is prepared by heating 2 parts of (yellow) corallin and 1 part of aqueous ammonia (sp.gr.=0·91) in an autoclave at 125°–140°, until a test shows the desired shade; the product is then poured into water acidified with sulphuric acid.

Pæonin is a dark-red amorphous mass, with a green metallic lustre, and is a mixed product containing among other compounds some pararosaniline. It is insoluble in water, but soluble in alcohol and alkalis, yielding purple-red solutions; acids do not affect the colour of its solutions. With wool and silk it gives shades intermediate between those of magenta and cochineal.

Closely related to aurin is **benzaurin** (*phenolbenzeïn*) $C_{19}H_{14}O_2$ or $\begin{matrix}C_6H_5\\OH{\cdot}C_6H_4\end{matrix}\!\!>\!C:C_6H_4:O$ obtained by gently heating 1 mol. of benzotrichloride with 2 mols. of anhydrous phenol, removing excess of phenol by steam distillation, extracting the residue with sodium bisulphite, and precipitating the filtrate with hydrochloric acid (Doebner, Ber. 12, 1462; compare Homolka, Ber. 18, 988). It crystallises in brick-red crystals, melts at about 100°, is insoluble in water, but soluble in alcohol, ether, and acetic acid. Alkalis dissolve it, yielding violet solutions. The *acetyl-* derivative melts at 119°. On reduction with zinc and hydrochloric acid, benzaurin is converted into dihydroxytriphenylmethane $C_{19}H_{16}O_2$.

Resorcinolbenzein $C_{38}H_{30}O_9$ (Doebner, Ber. 13, 610; Annalen, 217, 234; Aktieng. f. Anilinfab. in Berlin, D. R. P. 4322; E. P. 728 of 1878) is obtained by heating 1 mol. of benzotrichloride and 2 mols. of resorcinol at 180°–190°. It crystallises in large violet-red prisms, appearing yellow by transmitted light, is insoluble in water, ether, and benzene, has a yellowish-green fluorescence in dilute alcoholic solution, and yields a *bromo-* derivative which is sparingly soluble in all ordinary solvents, and dyes wool and silk in shades similar to those produced by eosin.

Rosolic acid (*rosaurin*) $C_{20}H_{16}O_3$ or $\begin{matrix}OH{\cdot}C_6H_4\\OH{\cdot}C_6H_3(CH_3)\end{matrix}\!\!>\!C:C_6H_4:O$ is formed by diazotising rosaniline (Caro and Wanklyn, Chem. News, 14, 37; compare Zulkowsky, Monatsh. 16, 395).

Preparation.—500 grams of rosaniline are dissolved in 1½ litres of concentrated hydrochloric acid diluted with 1½ litres of water, and the filtered brownish-yellow solution diluted with 150 litres of water is treated with a dilute solution of sodium nitrite until the rosaniline has

almost but not quite disappeared. The whole is then heated gradually to boiling, and filtered after the evolution of nitrogen has ceased. On cooling, rosolic acid separates in lustrous brownish-green crystals, and is purified by dissolving in soda ley, saturating the solution with sulphur dioxide, filtering and precipitating the compound by addition of a mineral acid to the nearly colourless filtrate (Caro and Graebe, Annalen, 179, 192).

Properties.—Rosolic acid crystallises from dilute alcohol in ruby-red crystals, or in greenish scales with a metallic lustre, does not melt at 270°, and is insoluble in benzene and carbon bisulphide, very sparingly soluble in water, soluble in ether and acetic acid, and readily soluble in alcohol. In alkalis it dissolves with a red colour, which in very thin layers is bluish-red, and in thick layers is yellowish-red. In dilute solution the colour change from pale yellow to red on the addition of alkali is sufficiently sensitive to admit of the use of the acid as an indicator (Thomson, Chem. News, 47, 184). It is a feeble acid, and yields an unstable ammonium salt, crystallising in steel-blue needles. Bromine in acetic acid solution converts it into *tetrabromorosolic acid* $C_{20}H_{12}Br_4O_3$, which crystallises in lustrous green scales, dissolves in alkalis with a violet colour, and with reducing agents yields the *leuco-* compound. When heated with acetic anhydride at 150°–200°, it forms, among other compounds, triacetylleucorosolic acid (m.p. 148°–149°); *leucorosolic acid* $C_{20}H_{18}O_3$ itself being obtained by reducing rosolic acid either with sodium amalgam or with zinc-dust and soda ley (Caro and Graebe, *l.c.*).

A colour reaction for rosolic acid has been described by Alvarez (Ann. Chim. anal. 12, 9). To obtain it, 0·05–0·1 gram, with 0·2–0·3 gram of sodium peroxide, is mixed with 5 c.c. of alcohol, and after 4–6 minutes, 15 c.c. of water are added, when an intense purple colouration is obtained which is not destroyed by water.

Azulin or **Azurin.** Blue colouring matters to which these names have been given are obtained by heating (yellow) corallin with aniline (D. and S. Annalen, 166, 294; Guinon, Marnas and Bonnet, *l.c.*) or rosolic acid with aniline or various diamines. By substituting phenylhydrazine or other hydrazines for aniline, red dyes known as **rhodazines** are obtained (Ville, D. R. P. 98436; Eng. Pat. 16039, 27775 of 1896; D. R. P. 100555 of 1896), and analogous bluish-red dyes are formed when aurintricarboxylic acid (*v. supra*) or aurincarboxylic acid (Vidal, Eng. Pat. 5535, 5689, of 1897) are substituted for corallin or aurin.

The hexamethoxy- derivatives of aurin and rosolic acid are described under EUPITTONIC ACID (*q.v.*). W. P. W.

AURUM MUSIVUM or **MOSAICUM.** *Mosaic gold.* Made by triturating an amalgam of 2 parts tin and 1 of mercury with 1 part sal ammoniac and 1 of sulphur, and subsequently subliming. Used as a bronzing powder for plaster figures (*v.* BRONZE POWDERS).

AUSTENITE. A solid solution of carbon in iron, of variable composition; is a constant constituent of steels containing 1·1 p.c. of carbon or more when cooled rapidly from a temperature of 1100°–1500°. It may be obtained pure by quenching a steel containing 0·93 p.c. carbon and 1·67 p.c. manganese from 1050° in ice-water (Maurer, Métallurgie, 1909, 6, 33). Steels containing 13 p.c. of manganese or 25 p.c. of nickel contain only austenite, and are soft and non-magnetic.

Under the microscope austenite is recognised by its softness as compared with '*martensite*,' with which it is usually associated; by its structureless appearance and by the brightness of an etched, polished section (Le Chatelier, Revue de Métallurgie, 1904).

AUTAN. A mixture of solid (polymerised) formaldehyde and the dioxides of barium or strontium, used in the disinfection of living-rooms. On mixing the powder with water, a rapid disengagement of formaldehyde vapour, mixed with oxygen, occurs.

AUSTRALENE *v.* TURPENTINE.

AUSTRIAN CINNABAR. *Basic lead chromate* (*v.* CHROMIUM).

AUTOCLAVE. An apparatus constructed on the principle of Papin's digester, for heating liquids at temperatures above their boiling-points. Autoclaves are usually made of cast-iron or steel, occasionally of copper, and in some cases of sheet-iron or steel. Cast-iron autoclaves are sometimes strapped with steel rings for greater security. They are often enamelled or lined with sheet-tin, lead, copper, or zinc. Metallic linings are now soldered rigidly to the surface of the autoclave. They are fitted with a pressure gauge and safety valve, and tubes for the insertion of thermometers, and are usually closed by a screw or flanged cover, working against a leaden washer, and are heated either by the circulation of hot oil or in a bath of molten lead. As they have frequently to sustain pressures of from 20 to 30 atmos., they are tested before use by hydraulic pressure. Occasionally they are provided with agitators working through stuffing boxes, in order to ensure thorough mixing of the contents when heated.

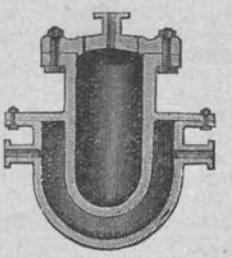


FIG. 1.

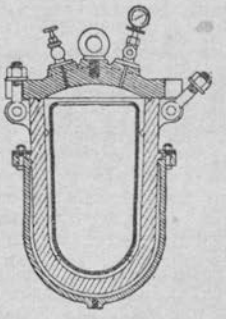


FIG. 2.

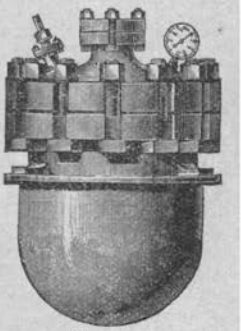


FIG. 3.

Fig. 4 shows a method of withdrawing portions of the contents of an autoclave, or

adding liquid without removing the cover, when the apparatus is in use. The three-way valve A is adjusted so as to prevent passage through the pipe *e*. In order to withdraw a sample, the three-way cock B is made to communicate with *b* and *d*, and the valve A turned with a jerk so as to connect *e* with *b*; the sample is then withdrawn at *d*. To completely remove the charge the valve A is left open for some time. In working without pressure the air-cock C is opened, and communication established between

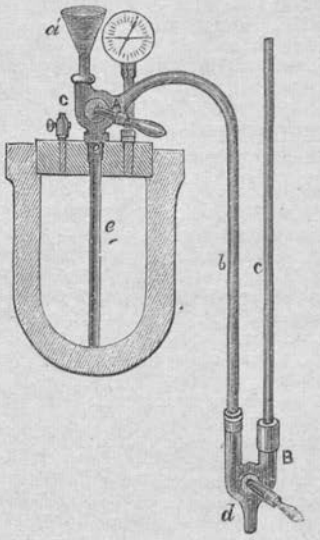


FIG. 4.

b and *c* and *a'* and *b*; *b* and *c* are then filled with liquor identical in constitution with that contained in the apparatus obtained from a previous operation. The contents of the vessel are then removed by restoring the communication between *e* and *b* and *b* and *d*. To introduce liquor into the apparatus without removing the cover, the air-cock C is opened, and the funnel *a'* made to communicate with the pipe *e* by regulating the valve A.

Sometimes it is more convenient, as shown in Fig. 2, to provide a loose container for the substance under treatment. J. W. H.

AUTOLYSIS. A physiological term signifying self-destruction, and used to indicate the destructive changes (apart from putrefaction due to micro-organisms) which occur in cells after death or removal from the living body. These changes are due to the action of intra-cellular enzymes, and are analagous to those which occur in digestion; indeed the term auto-digestion is sometimes employed. The study of such changes is important because it is believed that the change after death, when the cells are still 'surviving' for a time, are identical with those which occur during life and result in the formation of waste substances, the products of vital activity. During life, however, the destructive changes are counterbalanced by changes in the opposite direction by which the cells build themselves up from food materials to repair their wear and tear. Assimilation of this kind is obviously impossible after death.

AUTUNITE or **CALCO-URANITE.** A mineral consisting of hydrated phosphate of uranium and calcium $Ca(UO_2)_2P_2O_8{\cdot}8H_2O$, which within recent years has been somewhat extensively mined as an ore of uranium and radium. It is a member of the isomorphous group of minerals known as the 'uranium micas,' which crystallise in square, tetragonal (or very nearly square, orthorhombic) plates with a perfect micaceous and pearly cleavage parallel to their surface. In the orthorhombic autunite the colour is characteristically sulphur-yellow, or sometimes with a greenish tinge, so that this mineral is readily distinguished from the emerald-green torbernite or cupro-uranite. Sp.gr. 3·1; H. 2–2½. It occurs as an alteration product of pitchblende, and is often found as a scaly encrustation on the joint-planes of weathered granite or gneiss. The more important localities are St. Symphorien, near Autun in France (hence the name autunite); St. Just, Redruth, and Grampound Road in Cornwall; Johanngeorgenstadt and Falkenstein in Saxony; Black Hills in South Dakota; and Sabugal, near Guarda in Portugal. At the last-named locality several mines have recently been opened up; the crude ore is here leached with sulphuric acid, and the extracts sent to Paris for further treatment. L. J. S.

AVA or *Kava-kava.* The root of *Piper methysticum* (Forst, f.), growing in the islands of the Pacific. It is taken as an intoxicant by the natives, and is used as a drug on the Continent. It is often adulterated with matico and annatto (Pharm. J. [3] 7, 149).

AVENTURINE or **AVANTURINE.** A variety of quartz found at Capa de Gata, Spain, spangled throughout with minute yellow scales of mica, is known as aventurine quartz. An aventurine felspar or sunstone is found at Tvedestrand, Norway. It is used for ornaments.

Artificial aventurine, or *glass*, or *gold flux*, was manufactured for a long period at the glass-works of Murano, near Venice. It may be prepared by adding to 100 parts of a not too refractory glass, 8 to 10 parts of a mixture of equal parts of ferrous and cuprous oxides, and allowing the mixture to cool very slowly so as to facilitate the formation of crystals.

Aventurine glaze for porcelain, invented by Wöhler (Annalen, 70, 57), is prepared by finely grinding 31 parts Halle kaolin, 43 quartz sand, 14 gypsum, and 12 porcelain fragments; making the whole into a paste with 300 parts water, and adding successively 19 parts potassium dichromate, 47 lead acetate, 100 ferrous sulphate, and sufficient ammonia to precipitate the whole of the iron. After the soluble potash and ammonium salts have been washed out, the glazing is ready for use.

AVIGNON GRAINS. The seeds of *Rhamnus infectorius*, employed in dyeing for the production of yellow colours (*v. Rhamnin*, art. XANTHORHAMNIN).

AVOCADO PEAR or **ALLIGATOR PEAR.** The fruit of *Persea gratissima*, a tropical product. The fruit, which usually weighs from 4 to 6 oz., consists of rind (about 8 p.c.), flesh (67 p.c.), and a large 'stone' or 'pit' (about 25 p.c.). According to Prinsen-Geerlings (Chem. Zeit. 1897, 21, 715), the flesh contains:

Glucose	Fructose	Saccharose	Total sugar
0·40	0·46	0·86	1·72

The flesh, which has a nut-like flavour, is usually eaten with pepper and salt. An analysis, made by Jamieson (Chem. News, 1910, 102, 61), gave:

Water	Ether extract	Protein	Sugar	Fibre	Ash
66·9	10·6	5·7	1·1	4·0	2·0

The ether extract was green, and contained about 4 p.c. of resins. After their removal, an oil, resembling that of bergamot, was obtained, which had an iodine value of 29·9, and saponification value of 207. H. I.

AVOCADO PEAR, OIL OF. An oil obtained from the oleaginous fruit of the *Persea gratissima*. Hofmann stated that for the purposes of the soapmaker this oil would be as valuable as palm oil.

AWAL or *Tarwar*. An Indian drug, the bark of *Cassia auriculata* (Linn.) (Dymock, Pharm. J. [3] 7, 977).

AWLA *v.* AMLAKI.

AXIN. A waxy secretion of a Mexican rhynchotrous insect *Llaveia axinus* which feeds on *Spondias lutea*, *Xanthoxylum Clava-herculis*, and *X. pentanome:* has the consistence of butter, the smell of rancid fat, and a yellow colour. Melts at 38°, and is soluble in hot alcohol and ether. Rapidly absorbs oxygen from the air, becoming brown, hard and insoluble in alcohol and ether. Is readily saponified, yielding *axinic acid* and glycerol. It resembles Japan lac and forms an excellent lacquer for wood, metals, and pottery (Bocquillon, J. Pharm. Chim. 1910, 2, 406; J. Soc. Chem. Ind. 29, 1320).

AZADIRACHTA, *Margosa,* or *Nim.* The bark of the nim tree, *Melia indica* (Brandis) [*M. Azadirachta*], is commonly used in India as a tonic and febrifuge. It contains a bitter resin. An oil, used in medicine and for burning is expressed from the seeds, which on saponification yielded 35 p.c. of fatty acid melting at 30°, and 65 p.c. melting at 44°.

AZELAIC ACID. *Lepargylic acid.* $CO_2H\cdot(CH_2)_7\cdot CO_2H$. It is obtained by oxidising Chinese wax (Buckton, J. 1857, 303), cocoanut oil (Wirz, Annalen, 104, 261), or castor oil (Arppe, Annalen, 124, 86) with nitric acid; by the oxidation of oleic acid with potassium permanganate and caustic potash (Ehmed, Chem. Soc. Trans. 1898, 627), and by the oxidation of keratin (horn shavings) with permanganate (Lissizin, Zeitsch. physiol. Chem. 1909, 226). It is formed together with other products when fats or oleic acid become rancid (Scala, Chem. Zentr. 1898, i. 439). It has been synthesised from pentamethylene bromide and sodium acetoacetate (Haworth and Perkin, Chem. Soc. Trans. 1894, 86), and has been obtained by decomposing the ozonide of oleic acid (Molinari and Soncini, Ber. 1906, 2735; Harries and Thieme, *ibid.* 1906, 2844; Molinari and Fenaroli, *ibid.* 1908, 2789). It is best prepared by oxidising with potassium permanganate an alkaline solution of ricinoleic acid obtained by the hydrolysis of castor oil (Maquenne, Bull. Soc. chim. 1899, (iii.) 21, 106; Hazura and Grüssner, Monatsh. 9, 475). Azelaic acid crystallises in colourless plates, m.p. 106·2° (Massol, Bull. Soc. chim. [3] 19, 301), and is readily soluble in alcohol, less soluble in water or ether. By heating azelaic acid with soda lime, *azelaone* (*cyclononanone*) $C_8H_{14}O$, b.p. 205° (*circa*), is obtained (Miller and Tschitschkin, Chem. Zentr. 1899, ii. 181); Harris and Tank (Ber. 1907, 4555) have shown that a complex mixture of cycloketones is obtained by distilling the calcium salt of azelaic acid. *Azelaic anhydride* is obtained by heating azelaic acid with 7–8 pts. of acetyl chloride. It melts at 56°–57° (Étaix, Ann. Chim. Phys. [7] 9, 399).

AZELAONE *v.* AZELAIC ACID.

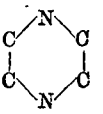
AZIDINE BLACK, -BLUE, -BORDEAUX, -BROWN, -FAST RED, -FAST SCARLET, -GREEN, -ORANGE, -PURPURINE, -YELLOW, -VIOLET, -WOOL BLUE *v.* AZO- COLOURING MATTERS.

AZIMINOBENZENE *v.* DIAZO COMPOUNDS.

AZIMINONAPHTHALENES *v.* DIAZO COMPOUNDS.

AZINES (Quinoxalines). Azonium bases, and colouring matters derived from them.

Definition.—The term 'azines' has been given to a group of organic bases, which contain in their molecule as an intrinsic part of their constitution a heterocyclic hexagonal ring, built up of four carbon and two nitrogen atoms, arranged in such a manner that the nitrogen atoms stand in para-position to each other, whilst the four carbon atoms are disposed in two pairs between them, thus:



The term 'azine,' first proposed by Merz, is not happily chosen, and is even misleading, as it enters into the names of other nitrogen compounds of a different constitution, such as the hydrazines.

The name 'quinoxaline' was given by Hinsberg to compounds which also correspond with the above definition. It was, therefore, considered for some time as synonymous with the word 'azine,' which latter was, however, more frequently used. In later years it has become customary to distinguish between the two terms, and to use them for the two tautomeric forms in which these bases occur (*see Theory*).

The name 'azonium bases' has been given by Witt to a class of organic bases, derived from the azines by the linking of an organic radicle to one of the nitrogen atoms, whereby this atom passes from the trivalent into the pentavalent state, a process which results in a very marked change of the properties of the substance.

Both the azines and azonium bases possess the nature of powerful chromogens, the heterocyclic ring above mentioned being endowed with strong chromophoric properties. Being highly basic and capable of assuming a quinonoid structure (*see Theory*), they, and especially the azonium bases, possess to some extent the nature of dyestuffs, which is, however, much more strongly developed by the introduction of separate auxochromic groups. A very large number of powerful colouring matters of great intensity, variation, and purity of shade may thus be obtained, some of which have acquired considerable practical importance. According to their constitution, which is in almost all cases completely cleared up, they have been classified into groups, which have received the names

eurhodines, eurhodols, safranines, safranols, aposafranines, indulines, and fluorindines.

The investigation of the azines and their derivatives, which was accomplished by a number of chemists during the last 20 years of the nineteenth century, has been of considerable importance in the development of our present views on the constitution of colouring matters, and especially in the adoption of the modern quinonoid structural formulæ for the great majority of them.

History.—The two simplest and most typical members of the azine group, diphenazine and dinaphtazine, have been known for many years as 'azophenylene' (Claus and Rasenack, 1873; Annalen, 168, 1) and 'naphtase' (Laurent, 1835; Ann. Chim. Phys. 59, 384), but their constitution was not properly understood and their importance not recognised. Merz (1886, Ber. 19, 725) finally proved the constitution of the former, which had been insufficiently substantiated by Claus, and proposed for it the name diphenazine; Witt (1886, Ber. 19, 2791) determined the true nature of 'naphtase.' In 1884 Hinsberg (Ber. 17, 319) described a general method for preparing his quinoxalines, which proved most fruitful in the further development of the subject. Other general methods were discovered by Witt, Merz, Japp, Ullmann, and others.

The first eurhodines were prepared by Witt in 1879 and 1885. He recognised that they formed a new class of dyestuffs, and also that they were related to the safranines. He determined their constitution in 1886 (Ber. 19, 441) by showing that they are the amino- derivatives of the azines or quinoxalines. At the same time he discovered the first eurhodol. The natural consequence of this discovery was the clearing up of the nature of the safranines, which were recognised in the same year simultaneously and independently by Witt, Nietzki, and Bernthsen as diamino- derivatives of the (then hypothetical) azonium bases. The first representative of this new class of bases was prepared in 1887 by Witt (Ber. 20, 1183).

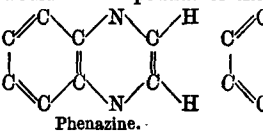
The subject was now taken up and rapidly advanced by many chemists, amongst whom Nietzki and his collaborators, Kehrmann, Ullmann, and their collaborators, may be cited. Otto Fischer and Hepp also did a considerable amount of work in this domain, and especially in the investigation of the indulines and aposafranines.

The typical indulines and safranines have been discovered by purely empirical methods in the early days of the colour industry. The simplest representative of the group, *phenosafranine*, was prepared by Witt in 1877. Its phenylated derivative is *mauveïne*, the first artificial dyestuff prepared by W. H. Perkin in 1856.

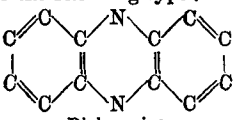
Theory.—It has been already stated that the essential part of the molecule of an azine is the heterocyclic ring consisting of two atoms of nitrogen and four of carbon. Each of these six atoms has three atomicities engaged in the formation of the ring; the nitrogen atoms have, therefore, no free atomicities left (so long as they remain in the trivalent condition), whilst each of the carbon atoms has one atomicity free to be saturated by hydrogen or another monovalent element or radicle. The simplest possible compound of the kind would thus have the formula $C_4N_2H_4$. It seems natural to suppose that it would be the prototype of all the azines.

Such a compound exists and is well known. It has received the name *pyrazine*. Many derivatives of it, formed by the substitution of its hydrogen atoms by monovalent organic radicles are also known; they form the large and well-investigated class of the ketine or aldine bases. But neither pyrazine itself (which in its properties resembles pyridine, to which it stands in the same relation as pyridine stands to benzene) nor the ketines show any resemblance to the typical azines. They exhibit no colourations, nor do they form any derivatives which have the nature of dyestuffs. For this reason pyrazine and the ketines are no longer considered as belonging to the azine group.

The characteristic properties of the azines only appear in compounds in which at least one other ring system is linked to the pyrazine ring, in such manner that one of the C_2-groups of the latter becomes part of an aromatic radicle. The process may be repeated. Thus the simplest representatives of the azine group would be compounds of the following type:—



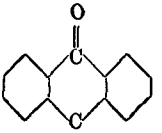
Phenazine.



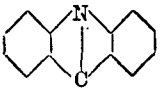
Diphenazine.

The nomenclature of the true azines has been chosen accordingly. The aromatic radicle or radicles linked to the central (or 'meso-') ring are prefixed to the syllables -azine.

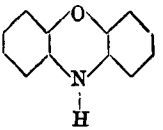
The azines are members of the aromatic series. If we consider them as such, we recognise at once a strong analogy to other substances which contain heterocyclic rings linked to aromatic radicles, such as:



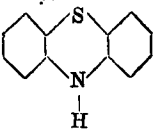
Anthraquinone.



Acridine.



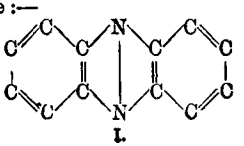
Oxazine.



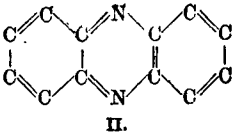
Thiazine.

all of which are chromogens, like the azines.

If we consider the manner in which the six atomicities of the two nitrogen atoms contained in the meso- ring of an azine may be disposed, we recognise two possibilities which are represented in the following structural formulæ of diphenazine:—



I.



II.

Formula I. is the one first proposed by Claus for his 'azophenylene,' and by Merz for his azines; II., the one suggested by Hinsberg for his quinoxalines. Practically, there is no difference between azines and quinoxalines; they form one group; but it has been for a long time a matter of opinion which of the above formulæ was more adapted to the properties of these substances. Formula I. explains by its perfect symmetry the extreme stability of the azines, the fact that they may all be distilled without the slightest decomposition at extremely high temperatures. Formula II., on the other hand, is distinctly (ortho-) quinonoid, and consequently suggestive of chromogenic properties.

The existing difference of opinion as to the constitution of the azines has been finally disposed of by the admission that the azines are undoubtedly tautomeric, capable of assuming either of the constitutions I. and II., according to circumstances. In their free state, in which they are volatile and almost colourless, they possess the symmetrical (azine-) constitution I., whereas in their intensely coloured salts they have more probably the asymmetrical, quinonoid (quinoxaline-) constitution II. In the colouring matters derived from the azines, the case is frequently complicated by the fact that the auxochromic groups participate in the formation of the quinonoid constitution, which, by that means, may become *para-* as well as *ortho*-quinoid. Sometimes it is difficult to decide between the existing possibilities.

Synthetical methods for the production of azines, and their derivatives and description of some typical representatives of the group.

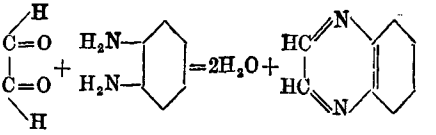
I. Azines. (*a*) *Synthetical methods.* (These will be referred to in the description of typical representatives by their number.)

1. By heating α-nitronaphthalene with powdered quicklime, Laurent (Ann. Chim. Phys. 59, 384) obtained dinaphthazine, which he called naphthase. Doer (Ber. 3, 291) and Klobukowski (Ber. 10, 573) modified the method by replacing the quicklime by zinc-dust. Schichuzky (J. R. 6, 2464) used lead oxide.

Wohl and Aue (Ber. 34, 2443) observed (1901) that nitrobenzene gives considerable quantities of diphenazine on being heated with strong caustic soda, a reaction which is practically identical with the one discovered by Laurent.

2. Claus and Rasenack (Annalen, 168, 1) obtained 'azophenylene' (diphenazine) by the dry distillation of orthoazobenzoic acid in the shape of its calcium or potassium salt. Claus proposed the azine formula for his product, but failed to afford convincing proofs for it.

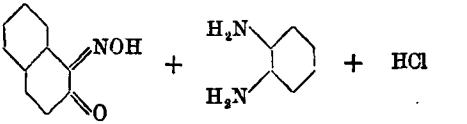
3. A general method of great applicability was indicated by Hinsberg (Ber. 17, 319; 18, 1228), who showed that whenever an *alpha-* or *ortho*-diketone reacts on an aromatic ortho-diamine, two molecules of water are given off and an azine is formed. The method was first applied to the production of phenazine:



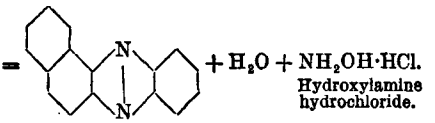
Glyoxal. o-Phenylenediamine. Phenazine (quinoxaline).

It works in most cases so well, that it has been recommended by its author (Annalen, 273, 343, 371) as the best method of identifying either an orthodiamine or an orthodiketone. Very small quantities of the ingredients are necessary, and the azine formed is easily recognised by its melting-point and sulphuric acid reaction.

Hinsberg's reaction may be extended to nitroso-β-naphthol, which is in reality the oxime of ortho-naphthaquinone. Ullmann and Heisler obtained (Ber. 42, 4263) naphthaphenazine by heating ortho-phenylenediamine hydrochloride with nitroso-β-naphthol:

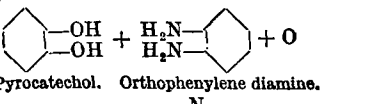


Nitroso-β-naphthol. Orthophenylene diamine.

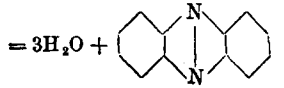


Naphthaphenazine. Hydroxylamine hydrochloride.

4. The method of Merz (Ber. 19, 725) is of less general application. It consists in the action of orthodihydroxyl- derivatives upon orthodiamines: the hydro- derivatives of the azines are formed, and these are oxidised by the oxygen of the air into the azines:



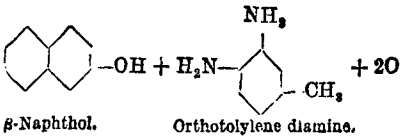
Pyrocatechol. Orthophenylene diamine.



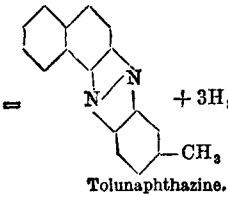
Diphenazine.

5. Early investigators had studied the reaction of ammonia under pressure upon benzoin (Erdmann, Annalen, 135, 181) and phenanthraquinone (Sommaruga, Monatsh. 1, 146). Japp and Burton showed that the free ammonia may be advantageously replaced by ammonium acetate, and proved that the 'ditolane azotide' and 'phenanthrene azotide' obtained were tetraphenylketine and diphenanthrazine. They generalised the method and applied it to β-naphthaquinone, from which they obtained dinaphthazine (Chem. Soc. Trans. 1887, 98).

6. Another mode of formation of the azines consists in the joint oxidation of a phenol, in which the *para-* position is no longer open to substitution, and aromatic orthodiamines. This method was discovered by Witt (Ber. 19, 917), who used it for the production of a new isomeride of tolunaphthazine by oxidising a mixture of β-naphthol and orthotolylene diamine:

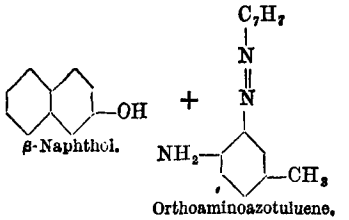


β-Naphthol. Orthotolylene diamine.

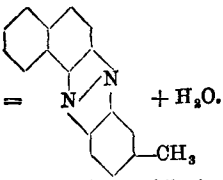


Tolunaphthazine.

7. An elegant modification of the above method was devised in 1905 by Ullmann and Ankersmit (Ber. 38, 1811), who heated β-naphthol with orthoaminoazotoluene. The latter takes up the hydrogen liberated in the reaction, yielding at the same time the necessary orthodiamine.

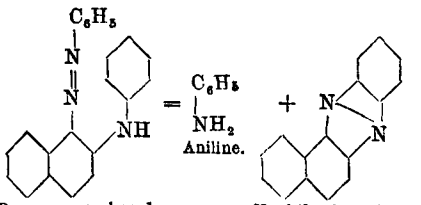


β-Naphthol. Orthoaminoazotuluene.



Tolunaphthazine.

8. A very peculiar mode of formation of these substances was discovered by Witt (Ber. 20, 571), who showed that the orthoazo- derivatives of secondary amines, and more especially of such amines containing the β-naphthyl- group, are decomposed by being heated with acids into the corresponding azine and amino- compound, thus :



Benzene-azo-phenyl-β-naphthylamine. Aniline. Naphthaphenazine.

The reaction is simple and easy, and gives, as a rule, excellent yields. It is in reality a condensation of the secondary amine into the corresponding azine by the dehydrogenating influence of the azo- group temporarily introduced for the purpose.

(*b*) *Generic characters of the azine group.* All azines have certain peculiar properties in common. As a rule, they are solid, well-crystallised compounds of white, pale yellow, or even orange colour, possessing a high melting-point, and boiling under atmospheric pressure at very high temperatures (in some cases approaching red heat) practically without decomposition. They sublime at temperatures below their boiling-point, and their vapours condense into voluminous aggregates of crystals.

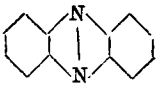
All the azines are bases which form salts with acids. The mono-acid salts, with the stronger mineral acids, may generally be obtained in a crystallised condition; but they are stable only in the presence of an excess of acid or in the absence of water, which easily decomposes them into their constituents. These salts are intensely coloured, a fact which justifies the inference that they contain the base in the quinonoid (quinoxaline) form. The hydrolytic action of the water is therefore accompanied by the tautomeric change into the symmetrical (azine) form. These salts, some of which have been analysed, invariably contain one equivalent of acid for one molecule of the base. The di-acid salts cannot be isolated, but evidence of their existence is given by the intense red, violet, or blue colourations exhibited by the solutions of azines in a great excess of strong acid, preferably sulphuric acid. If water be added to these solutions, a change takes place; the di-acid salt is decomposed, the yellow or orange mono-acid salt is formed, and, on further addition of a large excess of water, the free azine itself separates out in flakes. These striking colour reactions are highly characteristic, and form the best means of identifying the azines.

Notwithstanding these intense colourations, the azines are not applicable as dyestuffs. They are only to be considered as chromogens and suitable to produce colouring matters by the introduction of auxochromic groups into their molecules. They are thus strictly analogous to the other heterocyclic chromogens such as anthraquinone, acridine, oxazine, and thiazine.

There is, however, one group of azines to which all the rules and general characteristics given above cannot very well be applied. These are the 'Indanthrenes,' certain azines of the anthracene group, which, owing to their large molecule and very complicated constitution, possess properties quite different from all the other azines. They are intensely coloured and extremely valuable as dyestuffs if applied to the textile fibre by the 'vat process' like indigo. This peculiar mode of application brings them into close relationship with indigo, and they will therefore be treated in this work under INDIGO AND INDIGOID DYESTUFFS (*q.v.*).

(*c*) *Description of some typical representatives of the azine group.*

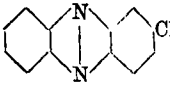
Diphenazine



(Claus, Annalen, 168, 1; Bernthsen, Ber. 19, 3256; Ris, Ber. 19, 2206; Wohl, Ber. 34, 2443) has been obtained by the methods 1, 2, and 4. It forms pale-yellow needles, of the m.p. 170°–171°, soluble in alcohol and most other solvents. It distils without decomposition. It dissolves

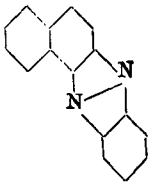
in strong acids, forming unstable salts of yellow and red colour.

Toluphenazine

$C_{13}H_{10}N_2 =$ 

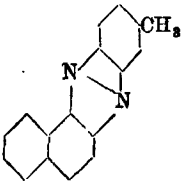
has been prepared by Merz (Ber. 19, 725) by the action of pyrocatechol on orthotolylenediamine (method 4). It is very similar to diphenazine. Its m.p. is 117°, its b.p. 350°.

Naphthaphenazine

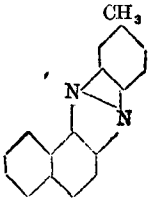
$C_{16}H_{10}N_2 =$ 

has been prepared by Witt (Ber. 20, 571). The best mode of obtaining it is by the decomposition, by acid, of the azo- compounds derived from phenyl-β-naphthylamine, but it has also been prepared by the action of β-naphthaquinone on orthophenylenediamine and by simultaneous oxidation of the latter and β-naphthol. It forms yellow needles, melting at 142·5°, distilling at a high temperature without decomposition, and dissolving in sulphuric acid with a reddish-brown colouration. On dilution, two sulphates crystallise from this solution. It is supposed that the formation of two series of monacid salts of this base is due to either of the two nitrogen atoms becoming pentavalent and saturated with the acid.

Tolunaphthazines $C_{17}H_{12}N_2$. Three substances of this formula are known, the isomerism of which has been discussed by Witt (Ber. 20, 577). One of these, melting at 179·8° has been prepared by the simultaneous oxidation (Ber. 19, 917) of orthotolylenediamine and β-naphthol (methods 6 and 7). Its constitution is expressed by the formula



It dissolves in sulphuric acid with a violet colouration. The other is formed by the decomposition by acids of the azo- derivatives of paratolyl-β-naphthylamine (Ber. 20, 577) (method 8). Its constitution is represented by the formula

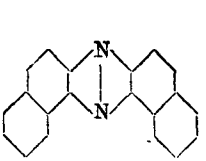


Its melting-point is 169°; its sulphuric acid reaction is similar to that of naphthaphenazine.

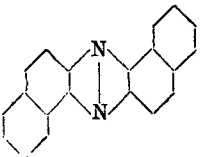
The third tolunaphthazine, discovered by Hinsberg (Annalen, 237, 343*a*, 371) (method 3), has been proved to consist of a molecular combination of the two preceding ones; its melting-point is 139°–142°.

Several other tolunaphthazines are theoretically possible. They have not, however, hitherto been prepared.

Dinaphthazines $C_{20}H_{12}N_2$. It has already been stated that Laurent's mysterious 'naphthase,' prepared by method 1, finally proved to be dinaphthazine. It is probable that Laurent's product was a molecular combination of two of the four isomeric dinaphthazines foreseen by theory. A similar mixture may be obtained by reacting with αβ-naphthylenediamine upon β-naphthaquinone (method 2). This method was used by Witt in his identification of Laurent's 'naphthase' (Ber. 19, 2791). For preparing the constituents of this mixture in a pure state the synthetical method 8 should be resorted to; it consists in the decomposition of the azo- derivatives of the two isomeric (α, β, and ββ)-dinaphthylamines (Matthes, Ber. 23, 1329 and 1333). The compounds thus obtained have the following constitutions and melting-points :—

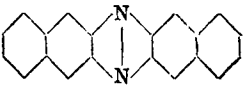


α, α, β, β. m.p. 285°–284°.

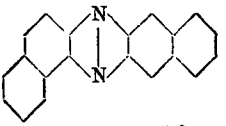


α, β, β, α. m.p. 242°–248°.

The two other possible isomerides:



β, β, β, β.



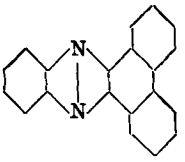
α, β, β, β. m.p. 240°

may be obtained from ββ-naphthylenediamine by the reaction of the two orthonaphthaquinones (method 2), but, so far, only the asymmetrical one has been prepared by Otto Fischer and Albert (Ber. 29, 2087).

Azines of the Phenanthrene group. Owing to the extreme facility and precision with which phenanthraquinone acts upon all orthodiamines, these azines are most easily prepared, and phenanthraquinone is commonly used for deciding the question whether any given aromatic diamine is an ortho- compound. A large number of azines has thus become known, of which only a few may be described as typical representatives of the group.

Phenanthraphenazine $C_{20}H_{12}N_2$ (isomeric with dinaphthazine) may be obtained by acting on orthophenylenediamine with either phenanthraquinone in an acetic acid solution (Hinsberg, Annalen, 237, 340), or with phenanthraquinone sodium bisulphite in an aqueous solution (method 2). It crystallises in pale-yellow

needles, melting at 217°, and dissolves in sulphuric acid with a beautiful red colouration. Its constitution is



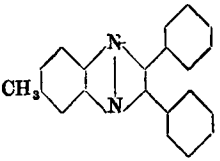
A similar substance may be obtained from orthotolylenediamine. It melts at 212°–213°.

Phenanthranaphthazine $C_{24}H_{14}N_2$ is easily obtained (Lawson, Ber. 18, 2426) from orthonaphthylenediamine and phenanthraquinone (*method 2*). It gives a violet colouration with sulphuric acid. M.p. 273°. The sulphonic acid derivatives of this substance, $C_{24}H_{13}N_2 \cdot SO_3H$, are obtained (Witt, Ber. 19, 1719; 21, 3485 *seq.*) by acting with an aqueous solution of phenanthraquinone sodium bisulphite upon the solutions of the various naphthylenediamine sulphonic acids in sodium acetate solution, acidulated with acetic acid. These sodium salts are soluble in pure water; very small quantities of alkaline salts are sufficient to precipitate them from these solutions.

Chrysotoluazine $C_{25}H_{16}N_2$ and **Chrysonaphthazine** $C_{28}H_{16}N_2$ have been prepared by Liebermann and Witt (Ber. 20, 2442) from chrysoquinone and the corresponding orthodiamines (*method 2*). The same authors obtained azine derivatives from the quinone of picene.

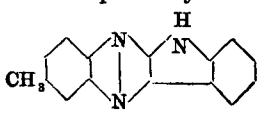
Tolustilbazine $C_{21}H_{16}N_2$ was discovered by Hinsberg, who described it under the somewhat misleading name 'Diphenyltoluquinoxaline' (Annalen, 237, 339). It is typical of the many azines which may be obtained by the action of benzil upon aromatic orthodiamines.

It separates in silvery leaflets from an alcoholic solution of benzil mixed with a solution of orthotolylenediamine (*method 2*). It melts at 111°, and dissolves with a crimson shade in sulphuric acid. Its constitution is expressed by the formula



The corresponding derivative of orthonaphthylenediamine was prepared by Lawson (Ber. 18, 2426).

Toluindazine $C_{15}H_{11}N_3$, the azine derivative of isatine, has been prepared by Hinsberg (Annalen, 237, 344) from orthotolylenediamine and isatin, by melting together the ingredients (*method 2*) and crystallising the product obtained from a mixture of alcohol and acetic acid. It forms yellow needles, melting at 290°, and dissolving in acids with a brownish-red colouration. Its constitution is expressed by the formula



A large number of other less important azines have been prepared in experiments made with a view to showing that certain compounds obtained by the authors were either orthodiketones or orthodiamines.

II. Colouring matters derived from azines (eurhodines and eurhodols).

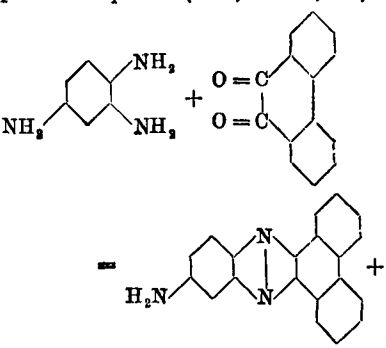
It has already been said that by the introduction of an auxochromic group, NH_2 or OH, into the molecule of an azine, the latter is transformed into a colouring matter. The amino-derivatives of azines containing either one or several amino- groups, are embraced by the generic name of *eurhodines*, whilst the name of *eurhodols* has been given to the phenolic (OH) derivatives of the azines. The following is an enumeration of the various methods by which eurhodines and eurhodols have been obtained:—

A. EURHODINES.

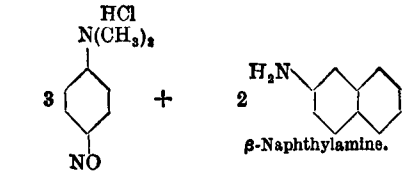
1. By heating together any orthamino-azo-compound and the hydrochloride of certain aromatic monoamines, such as, for instance, α-naphthylamine or α-aminoquinoline, preferably in a phenol solution, monoamino-azines (the eurhodines proper) are obtained. It was by this process that the first eurhodine was discovered by Witt in 1883 (Ber. 18, 1119; 19, 441) by heating orthaminoazotoluene with naphthylamine hydrochloride. In this reaction an orthodiamine is formed by the reduction of the amino-azo compound, which combines with α-naphthylamine, hydrogen being eliminated and absorbed by the amino-azo- compound still present.

$$\underset{\text{Orthotolylene-diamine.}}{C_7H_{10}N_2} + \underset{\text{α-Naphthyl-amine.}}{C_{10}H_9N} = 6H + \underset{\text{Typical eurhodine.}}{C_{17}H_{13}N_3}.$$

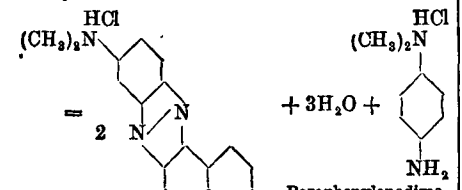
2. Another method of much greater applicability consists in reacting with α-diketones upon aromatic triamines, which contain two amino-groups in the ortho- position. Two molecules of water are eliminated for every molecule of eurhodine formed. Thus, for instance, a eurhodine was obtained from triaminobenzene and phenanthraquinone (Witt, Ber. 19, 445):



3. Another method of considerable applicability consists in heating together nitroso-amines (Witt, Ber. 21, 719) or quinonedichlorimides (Nietzki a. Otto, Ber. 21, 1598) with aromatic amines in which the para- position to the amino-group is occupied by some radicle. Thus, for instance, a eurhodine is formed by heating together nitrosodimethylaniline hydrochloride and β-naphthylamine, in an acetic acid solution:

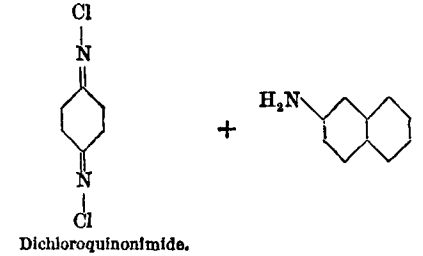


Nitrosodimethylaniline hydrochloride. β-Naphthylamine.

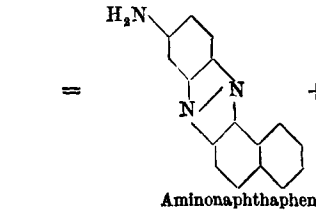


Dimethylaminonaphthaphenazine hydrochloride. Paraphenylenedimethyldiamine monohydrochloride.

and an analogous, though somewhat different reaction takes place if the nitrosodimethylaniline be substituted by dichloroquinonimide.



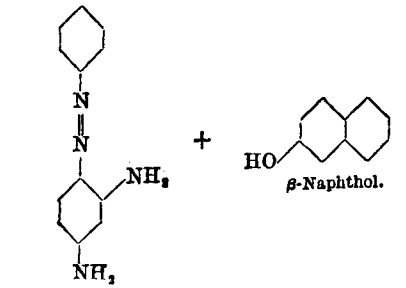
Dichloroquinonimide.



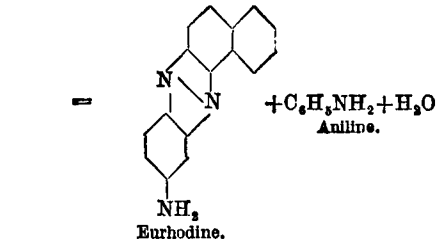
Aminonaphthaphenazine.

4. Eurhodines proper may also be obtained by the reduction (with ammonium sulphide) of nitro-azines. Thus, for instance, nitrophenophenanthrazine may be reduced into the eurhodine aminophenophenanthrazine (Heim, Ber. 21, 2306).

5. If certain azo- colours, such as chrysoïdine, be heated with β-naphthol, an eurhodine is formed: (Ullmann and Ankersmit, Ber. 38, 1812):

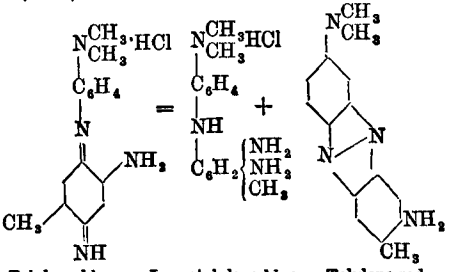


Chrysoidine. β-Naphthol.



Eurhodine. Aniline.

6. Diaminoazines are formed by the decomposition of certain indamines when their solutions are boiled for a certain time. Thus tolylene blue, the indamine produced by the action of nitrosodimethylaniline hydrochloride upon metatolylenediamine, is decomposed if its solution be boiled for some time, dimethyldiaminotoluphenazine (tolylene red) being the principal product of this reaction (Witt, Ber. 12, 931):



Tolylene blue. Leucotolylene blue. Tolylene red (dimethyldiaminotoluphenazine).

7. Di- and polyamino- azines may also be prepared by the oxidation of orthodiamines and of polyamines containing two amino- groups in the ortho- position. Thus O. Fischer and E. Hepp proved (Ber. 22, 355) that the red substance which is formed by the oxidation of orthophenylenediamine and which has been observed by many investigators (Griess, Ber. 5, 202; Salkowski, Annalen, 173, 58; Rudolph, Ber. 12, 2211; Wiesinger, Annalen, 224, 353), is nothing else than diaminophenazine. And Nietzki and Müller obtained (Ber. 22, 447) by oxidising tetra-aminobenzene with a current of air tetraaminophenazine. Aminooxyphenazines may sometimes be found as by-products in this reaction (Ullmann and Mauthner, Ber. 35, 4302 and *ibid.* 36, 4026).

B. Eurhodols.

These may likewise be prepared by various methods.

1. The sulphonic acids of azines, fused with potash, readily yield the corresponding oxyazines or eurhodols (Witt, Ber. 19, 2791). For instance:

$$C_{24}H_{13}N_2SO_3Na + 2NaOH$$

Sodium naphthaphenanthrazinesulphonate.

$$= C_{24}H_{13}N_2ONa + Na_2SO_3.$$

Phenanthranaphthaeurhodol.

2. Several eurhodines (amino-azines) yield the corresponding eurhodol on being heated under pressure with strong acids, a hydrolysis taking place in the circumstances (Witt, Ber. 19, 444):

$$C_{17}H_{11}N_2 \cdot NH_2 + H_2O = NH_3 + C_{17}H_{11}N_2 \cdot OH.$$

Typical eurhodine. Eurhodol.

3. Diazo-azines, on being boiled with water, yield the corresponding eurhodols; on being boiled with alcohol they yield the alkyl ethers of these eurhodols (Witt, Ber. 19, 444):

$C_{17}H_{11}N_2{\cdot}N : N{\cdot}Cl + H_2O$
Diazoeurhodine chloride.
$= HCl + N_2 + C_{17}H_{11}N_2OH.$
Eurhodol.

$C_{17}H_{11}N_2{\cdot}N : N{\cdot}Cl + C_2H_5OH$
$= HCl + N_2 + C_{17}H_{11}N_2OC_2H_5.$
Ethyleurhodol.

The following is an enumeration of those of the eurhodines and eurhodols which have been more closely investigated, the properties of which are typical for the whole class of colouring matters:—

Typical eurhodine $C_{17}H_{13}N_3$ (Witt, Ber. 19, 445). The mode of formation of this substance has already been given (Section A, 1). It is best prepared by heating to 130° equal molecules of orthoaminoazotoluene, of the melting-point 118·5°, and α-naphthylamine hydrochloride, dissolved in phenol until the colour of the mixture, which is at first of an emerald green, has changed into a brilliant scarlet. The mixture is now treated with a large quantity of toluene, when the hydrochloride of the new dyestuff is precipitated in a crystalline state. By recrystallisation from water acidified with hydrochloric acid, it may be obtained in a pure state. From the pure hydrochloride the free eurhodine base is precipitated by alkalis or ammonia in the form of a yellow powder, which may be recrystallised from aniline. Thus prepared, it forms glistening yellow prisms and needles of a dark-brown colour. It dissolves in ether with a yellow colour and a magnificent green fluorescence, which is characteristic of all the members of this group of dyestuffs. Eurhodine forms three series of salts, of which, however, only those with one molecule of acid are fairly stable, whilst those containing more acid are decomposed by the addition of water. It is to the formation of these various salts that the peculiar change of colour is due which is observed on adding water to a solution of eurhodine in concentrated sulphuric acid. This solution is of a cherry-red colour. On adding a small quantity of water the colour changes to a fine emerald green, whilst still more water produces the scarlet shade of the normal sulphate. This change of colour, which is observed with all the eurhodines, links them to their parent-substances, the azines, which exhibit similar curious phenomena, and also to the safranines.

The normal salts of eurhodine are well crystallised and of a bronzed copper colour when solid. In solution they exhibit a bright scarlet tint which they communicate to the fibre. These normal salts are, however, partially decomposed by an excess of water, the free eurhodine base being regenerated. The same takes place if fibres dyed red with eurhodine be washed. The scarlet shade is gradually replaced by the yellow shade of the free eurhodine base. For this reason eurhodine has not found an application in the industry of artificial dyestuffs.

Aminonaphthaphenazine $C_{16}H_{11}N_3$ has been obtained by Nietzki and Otto (Ber. 21, 1598) from β-naphthylamine and dichloroquinonimide (Ullmann and Ankersmit, Ber. 38, 1811). It crystallises in dark-yellow needles. Its salts are of a crimson colour. Its solution in sulphuric acid changes by the addition of water from reddish-brown through green into red. It forms a diazo- compound which, when boiled with alcohol, yields the ordinary naphthaphenazine, of the melting-point 142·5°. The following compound is its dimethyl derivative:—

Dimethylaminonaphthaphenazine $C_{18}H_{15}N_3$ (Witt, Ber. 21, 719). This eurhodine, the formation of which has been described under Section A, 3, may easily be prepared in quantity by heating together 20 parts nitrosodimethylaniline hydrochloride and 10 parts β-naphthylamine with 50 glacial acetic acid; the reaction sets in below 100°, and is apt to become violent. The product changes to a fine violet colour. It is dissolved in water acidified with hydrochloric acid, and the filtered solution is precipitated by the addition of sodium acetate. The crude eurhodine which is thus precipitated may be purified by dissolving it in alcohol acidified with hydrochloric acid. From this solution the normal eurhodine hydrochloride crystallises in bronze-coloured needles. From these ammonia liberates the free eurhodine base in the form of a scarlet crystalline powder. It may be recrystallised from boiling xylene; it is thus obtained in magnificent crystals resembling magnesium-platinocyanide, melting at 205°.

The change of colour of a sulphuric acid solution of this eurhodine is not very marked, going from violet through black and green into violet. The ethereal solution of the free base exhibits the brilliant fluorescence characteristic of all eurhodines.

Aminophenaphenanthrazine $C_{20}H_{13}N_3$. This eurhodine was prepared by Witt (Ber. 19, 445) and by Heim (Ber. 21, 2306) by the methods given under Section A, 2 and 4. It crystallises from toluene in short, thick, yellow prisms, melting at 279°.

Dimethyldiaminotoluphenazine; Tolylene red $C_{15}H_{16}N_4$. The formation of this compound by the spontaneous decomposition of tolylene blue has been described under Section A, 5. This eurhodine forms, in a pure state, orange crystals, which contain 4 mols. of water of crystallisation; at 150° this is given off and the anhydrous base remains as a dark-red powder. The hydrated base is soluble in ether with a pink colour and a beautiful orange fluorescence. The solution in concentrated sulphuric acid is green; on being diluted with water it changes through sky-blue into red. The normal (monacid) salts are perfectly stable and soluble in water with a pink colour. This solution dyes unmordanted or mordanted cotton and other fibres a pink which in darker shades deepens into a coppery red.

The production of this dyestuff has been patented (Otto N. Witt, D. R. P. 15272). The commercial product, which contains a certain amount of impurities, is sold under the name of 'neutral red.' It is chiefly used in calico-printing, and gives very fast and useful shades.

A similar product is prepared from the indamine which is formed by reacting with nitrosodimethylamine hydrochloride upon metaphenylenediamine. It is embraced by the same patent and sold under the name of 'neutral violet.'

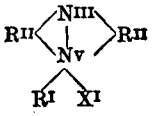
Typical eurhodol $C_{17}H_{11}N_3OH$ (Witt, Ber.

19, 444). This substance, the formation of which takes place according to the equation given under Section B, 2, forms small leaflets of a yellow or red colour which dissolve in concentrated sulphuric acid with a red colouration, and are reprecipitated from this solution by the addition of water. Caustic soda solution dissolves it with an orange shade. Thus it is shown that this eurhodol (like all compounds of the same class) exhibits both acid and basic properties, the latter being due to the azine group contained in their molecule.

Eurhodol $C_{24}H_{14}N_2OH$. α-Hydroxynaphthaphenanthrazine has been obtained (Witt, Ber. 19, 2791) by the method described under Section B, 1, by the fusion of naphthaphenanthrazine-α-sulphonic acid with caustic alkalis. Its solution in sulphuric acid is of a fine and intense indigo-blue; it changes very suddenly into red on the addition of water, the sulphate being precipitated. This substance is a yellow colouring matter which may be fixed on cotton with alum-mordant, like alizarin. Owing, however, to its costliness, it has not been brought into commerce. A large number of isomerides may be prepared by starting from the numerous sulpho- derivatives of orthonaphthylenediamine, transforming them into azinesulphonates by condensation with phenanthraquinone and into eurhodols by subsequent fusion with caustic alkalis.

III. **Azonium bases and safranines.** The azonium bases are a class of compounds of which our knowledge is very restricted, very few representatives of the class being at present known, and that rather imperfectly. They are, however, of importance, as it is now established beyond doubt that they are the parent substances of the very important class of dyestuffs known as safranines. Although the first artificial dyestuff, mauveine, was a true safranine, and although this group of compounds has been frequently under investigation, a correct view of their constitution had not been obtained until quite recently. According to the theory now universally adopted, all safranines are amino- derivatives of azonium bases, to which they stand in the same relation as the eurhodines to the azines. Hydroxy- derivatives of azonium bases have also been prepared and described under the name of safranols. They are, however, of no importance as colouring matters.

The azonium bases themselves, none of which has so far been obtained in a state fit for analysis, stand in the same relation to the azines as the ammonium bases to the amines. They are azines in which one of the nitrogen atoms has become pentavalent by being saturated with three organic radicles and one acid radicle, the connection with the second nitrogen atom being still preserved by the fifth valency of the pentavalent nitrogen atom. Thus the characteristic constitution of the azonium compounds may be expressed by the general formula



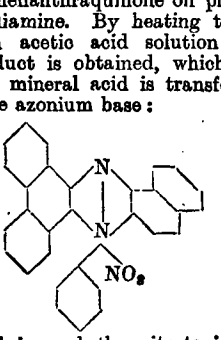
in which R^I and R^{II} represent mono- and divalent organic radicles, and X^I a monovalent acid radicle. The azonium bases are compounds which possess strong basic properties, and which, by the tenacity with which they retain their acid radicle, strongly resemble the ammonium bases. It is probable that the free azonium bases contain, like the ammonium bases, the hydroxyl group in the position X^I of the above general formula. The azonium bases and the dyestuffs derived from them are also capable of tautomeric changes, which lead to their assuming quinonoid structures. The nature of these changes is in many cases doubtful and too complicated to be fully discussed in this article.

The azonium bases are strongly coloured substances, but their dyeing properties are developed and brought to perfection by the introduction of amino- groups into their molecule. As the azonium bases theoretically possible are very numerous, and each of them is capable of producing very numerous isomeric mono- and polyamino- derivatives, the number of possible safranines is exceedingly large, and the number of those which have already been prepared is insignificant in comparison with that foreshadowed by theory.

Of the safranines which have hitherto been prepared, only a few are monoamino- derivatives of azonium bases. A few more are of doubtful or unknown constitution. The majority are asymmetric diamino- derivatives of azonium bases, containing one amino- group in one of the diatomic organic radicles (R^{II}, whilst the other is attached to the monoatomic radicle (R^I).

The true constitution of phenosafranine and its congeners has been recognised by Witt, who, after pointing out the analogy between the eurhodines and safranines (Ber. 18, 1119) and clearing up the constitution of the former (Ber. 19, 446), proved the latter to be asymmetric diaminoazonium bases (Ber. 19, 3121). Bernthsen had proposed (Ber. 19, 2690) somewhat earlier a symmetrical formula for the safranines based upon Witt's eurhodine researches. His view was subsequently adopted by some chemists, but the author of this article fails to see the force of the arguments adduced in support of it.

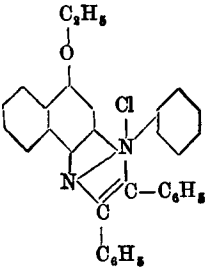
A. **Azonium bases.** 1. The typical compound was obtained by Witt (Ber. 20, 1183) by the reaction of phenanthraquinone on phenylorthonaphthylenediamine. By heating these ingredients in an acetic acid solution an intermediate product is obtained, which on treatment with a mineral acid is transformed into the salt of the azonium base:



If nitric acid is used, the nitrate is deposited in very fine crystals. It is sparingly soluble in water, readily soluble in spirit with a fine orange-red colouration. The hydrochloride dissolves in sulphuric acid with a violet tint, which changes into red on dilution with water.

2. If in this reaction the phenylorthonaphthylenediamine be replaced by phenylorthophenylenediamine, the resulting compound is a yellow dyestuff of considerable strength. It is manufactured and sold under the name 'Flavinduline' (1893).

3. A very similar compound was obtained by Otto N. Witt and Christoph Schmidt in 1892 (Ber. 25, 1017), by the reaction of benzil upon ethoxyphenylorthonaphthylendiamine. It was called ethoxyphenylnaphthostilbazonium chloride and has the constitution:



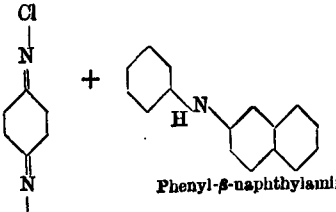
It is a beautiful yellow dyestuff, but too expensive to be prepared on a manufacturing scale.

B. **Safranines.** The various colouring matters belonging to this group have mostly been prepared by different synthetical methods, which may be classed in the following manner:—

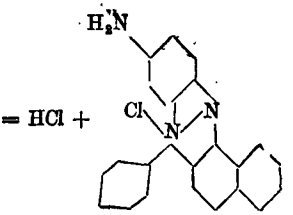
1. Reduction of the nitro- derivatives of azonium bases. By reacting with mononitrophenanthraquinone or dinitrophenanthraquinone on phenylorthonaphthylenediamine, nitro- and dinitro- derivatives of the above azonium base are obtained, which on reduction with ammonium sulphide yield reddish-violet colouring matters belonging to the safranine group (Witt, unpublished observations).

2. If the stilbazonium base obtained by Witt and Schmidt, or any of its congeners prepared from ethylated arylorthonaphthylenediamines be heated with ammonia, the ethoxy group is replaced by the amino- group and the corresponding safranines are formed. This is quite a general reaction (Witt and Schmidt, Ber. 25, 2003; Witt and v. Helmolt, Ber. 27, 2355; Witt and Buntrock, Ber. 27, 2362).

3. By the action of dichloroquinonimides upon secondary aromatic amines, in which the para- position to the amino- group is occupied, monoamino-azonium bases are formed (Nietzki and Otto, Ber. 21, 1598). The reaction, for instance, between dichloroquinonimide and phenyl-β-naphthylamine may be represented by the equation:

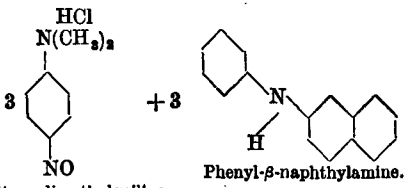


Dichloroquinonimide. Phenyl-β-naphthylamine.

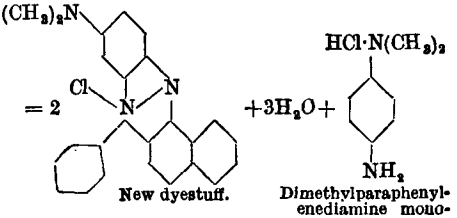


New dyestuff.

4. In a similar manner nitrosodimethylaniline (or any other nitroso-amine) reacts with phenyl-β-nnphthylamine (Witt, Ber. 21, 719):



Nitrosodimethylaniline hydrochloride. Phenyl-β-naphthylamine.



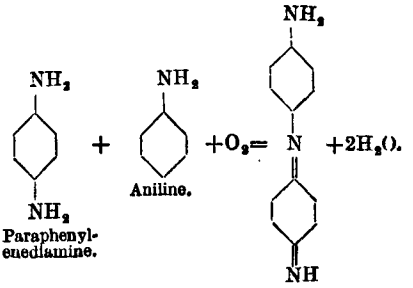
New dyestuff. Dimethylparaphenylenediamine monohydrochloride.

5. The safranines proper (asymmetric diaminoazonium bases) are formed by the joint oxidation of one molecule of diamine and two molecules of an aromatic monoamine. In this reaction fugitive indamines are formed as intermediate products; the process thus becomes strictly analogous to the formation of toluylene red and its congeners.

This is the process which is generally used in the manufacture of safranines, and it will therefore be fully explained.

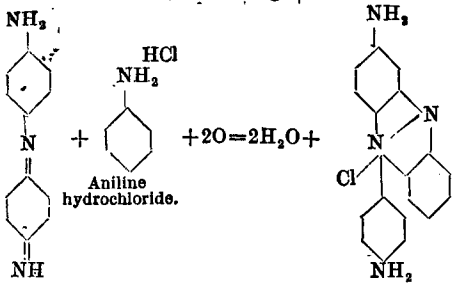
By the joint oxidation of an aromatic paradiamine with one molecule of an aromatic monoamine, an indamine is invariably formed (*v.* INDAMINES). If these indamines be oxidised in the presence of another molecule of an aromatic monoamine, a safranine is formed:

First Stage.

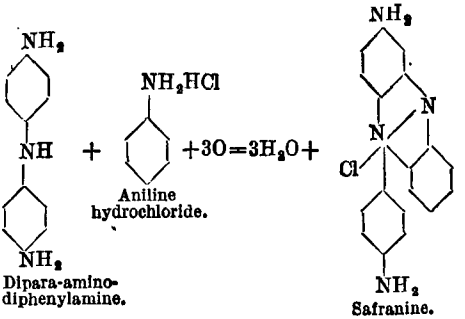


Paraphenylenediamine. Aniline. Indamine.

Second Stage.



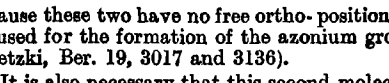
Indamine. Phenosafranine.



* Of course, any other paradiamine may be substituted for paraphenylenediamine, and any other monoamine for aniline. As, however, the formation of an indamine only takes place if the para- position to the amino- group be still free, it results, that at least one of the two molecules of monoamines must fulfil this condition. Thus the formation of a safranine from paraphenylenediamine takes place on oxidation of one molecule of the diamine with

(1) Two molecules of aniline.
(2) Two molecules of orthotoluidine.
(3) One of aniline and one of orthotoluidine.
(4) One of aniline and one of paratoluidine.
(5) One of orthotoluidine and one of paratoluidine; but it does not take place with one molecule of paraphenylenediamine and two of paratoluidine (Witt, J. Soc. Chem. Ind. 1882, 256).

On the other hand, the other of the two molecules of monoamines must have a free ortho-position in order to be capable of entering the reaction. Thus the indamine of the above formula forms safranines with all the primary aromatic monoamines of the benzene series, with the exception of one xylidine and of mesidine, of the respective formulæ



because these two have no free ortho- position to be used for the formation of the azonium group (Nietzki, Ber. 19, 3017 and 3136).

It is also necessary that this second molecule of monoamine be a primary base, whilst the one necessary for the formation of the indamine may be either primary, secondary, or tertiary, provided always that it possesses a free para-position.

6. It is evident that the general process described under 4 may be modified; thus, for instance, the dipara-amino- derivatives of secondary bases (being the leuco- compounds of indamines) may be oxidised together with one molecule of a primary aromatic monoamine, when a safranine is the result (see top of page, second column):

7. Another modification (Witt, Ber. 10, 873) consists in heating aminoazo- compounds with the hydrochlorides of aromatic monoamines. This is the oldest process for the manufacture of safranines. The mechanism of this reaction is simple. Part of the aminoazo- compound being reduced, a mixture of a paradiamine and a primary monoamine in molecular proportions is formed, which with the monoamine added in the shape of hydrochloride, is transformed into safranine by the dehydrogenating action of the remaining part of the aminoazo- compound. It is evident that the yield must be small in this process of manufacture, and such is actually the case.

8. An asymmetrical safranine has been obtained by the reduction of picryl-orthophenylenediamine (Kehrmann, Ber. 33, 3074).

9. Certain compounds belonging to the safranine group (mauveïne, &c.) are formed in a very complicated reaction by the oxidation of heavy aniline alone; on continued oxidation mauveïne is converted into a safranine (Perkin, Roy. Soc. Proc. 35, 717).

The following is an account of the more important and more thoroughly investigated safranines:—

A. Monamino- Derivatives of Azonium Bases.

1. **Aposafranine,** Monoaminophenylphenazonium chloride, has been obtained by Nietzki and Otto (Ber. 21, 1736; *see* also Annalen, 286, 188, and Ber. 30, 2624, and 33, 3078) from phenosafranine (*see* below) by diazotising one of its amino- groups, and eliminating it by means of alcohol. It is a red dyestuff of no practical importance, but very interesting as prototype of the induline group (*see* under Indulines).

2. **Red dyestuff** $C_{22}H_{16}N_3Cl$. Obtained by the action of dichloroquinonimide on phenyl-β-naphthylamine, was prepared by Nietzki and Otto (Ber. 21, 1598) by heating the ingredients in molecular proportion in alcoholic solution on the water-bath. The nitrate forms green needles or prisms which are soluble in water with a magenta-red colour. The hydrochloride dissolves in sulphuric acid with a red colouration, which on dilution changes through green into red.

3. **Violet colouring matter** $C_{24}H_{20}N_3Cl$. Prepared by Witt (Ber. 21, 719) by acting with 3 molecules of nitrosodimethylaniline hydrochloride in an acetic acid solution on 2 molecules of phenyl-β-naphthylamine. This is the dimethyl- derivative of the preceding substance.

The hydrochloride forms large black needles soluble in water, with a fine violet colour. The free base, $C_{24}H_{20}N_3 \cdot OH$, is liberated from the salts by caustic alkalis only. It is insoluble in water, soluble in alcohol, with a red colour and a fine orange fluorescence. It is sold as 'neutral blue.'

4. **Violet colouring matter** $C_{25}H_{22}N_3Cl$. Prepared by Witt (Ber. 21, 719) from paratolyl-β-naphthylamine in exactly the same manner as the preceding substance, of which this is the next homologue. Violet soft needles, resembling in their colour and reactions the phenyl-derivative.

The above substances have been patented (Otto N. Witt, D. R. P. 19224, dated Feb. 18, 1882).

5. **Basle blue** $C_{32}H_{29}N_4Cl$ is a fine blue dyestuff prepared (T. Annaheim, Ber. 20, 1371; Durand and Huguenin, Ger. Pat. 40886) by the reaction of nitrosodimethylaniline hydrochloride on the paratolylnaphthylenediamine which is formed by heating Ebert and Merz's dihydroxynaphthalene with paratoluidine hydrochloride. It forms a brown crystalline powder, soluble in water with a bluish-violet shade. In concentrated sulphuric acid it dissolves with a greenish-brown shade, which changes through green into violet on dilution.

6. **Azine green** $C_{30}H_{25}N_4Cl$ is formed by the reaction of nitrosodimethylaniline hydrochloride upon 2-6-diphenylnaphthylenediamine.

7. **Induline scarlet** $C_{19}H_{18}N_3Cl$, a very beautiful red dyestuff discovered by Schraube (D. R. P. 77226), and manufactured by the Badische Aniline and Soda-Fabrik, is really not an induline, but a safranine. It is prepared by melting together the hydrochloride of anilinazoethylparatoluidine and α-naphthylamine. The reaction is strictly analogous to the formation of the typical eurhodine.

B. Diamino- Derivatives of Azonium Bases.

1. **Phenosafranine** $C_{18}H_{15}N_4Cl$. Discovered by Witt (exhibited in Paris in 1878; and mentioned in the catalogue of Messrs. Williams, Thomas & Dower, closely investigated by Nietzki (Ber. 16, 464) and by Bindschedler (Ber. 13, 207; 16, 865).

It was with this compound that the mode of formation of the safranines and their chemical properties were definitely ascertained, chiefly by R. Nietzki, whose brilliant researches on this subject did much to clear up the chemistry of this group.

Phenosafranine is prepared by the joint oxidation of paraphenylenediamine and aniline. The mechanism of this process has already been discussed. A dilute aqueous solution of the normal hydrochlorides of these bases is used, and their oxidation is accomplished by adding potassium or sodium bichromate or manganese dioxide in the necessary proportion to the hot solution. The blue colour of the indamine which appears at first is immediately replaced by the red colour of the safranine formed. A certain quantity of insoluble dark by-products is always formed, but by careful work the yield of pure safranine may be raised to 70 p.c. of the theory. When the oxidation is finished, soda solution or chalk is added in order to precipitate the impurities, and the liquid is filtered. By adding a small amount of nitric acid and some sodium nitrate to the filtered solution, the nitrate of the safranine crystallises out; or the chloride may be prepared by adding common salt to the solution after acidifying it with hydrochloric acid. By repeated recrystallisation from water or alcohol, the phenosafranine is obtained in a state of purity, in the form of magnificent green needles. The *sulphate* forms blue needles. The platinum salt $(C_{18}H_{15}N_4Cl)_2PtCl_4$ forms insoluble shining leaflets. Phenosafranine forms a diacetyl- derivative on boiling with acetic anhydride in the presence of dry sodium acetate. It forms two diazo-derivatives, of which the first

$$C_{18}H_{13}N_3Cl \diagdown N : N \cdot Cl$$

is rather stable and soluble in water, with blue colouration. The other diazo- compound

$$C_{18}H_{11}N_3Cl \begin{cases} \diagup N : N \cdot Cl \\ \diagdown N : N \cdot Cl \end{cases}$$

is very unstable and of a green colour.

Phenosafranine dyes wool, silk, and cotton a magnificent pink. Its aqueous solutions are red and show no fluorescence, whilst alcoholic solutions show a marked greenish-yellow fluorescence. Phenosafranine dissolves in concentrated sulphuric acid with a green colouration which changes through blue into red on dilution, thus indicating the actual existence of the three series of salts foreshadowed by theory.

If phenosafranine or its homologues be diazotised and then combined with β-naphthol, beautiful basic blue dyestuffs are obtained, which are largely prepared and used for cotton-dyeing and calico-printing under the name of 'Indoine blue.'

The alkyl- derivatives of phenosafranine are interesting colouring matters, some of which have found an industrial application. They have not been prepared by introducing alkyl-groups into ready-formed safranine, but rather by direct synthesis from suitable raw materials. Each of them exists in two isomeric modifications, according to the amino- group into which the alkyl- group has been introduced. The two amino- groups of phenosafranine being asymmetric, and therefore not equivalent to one another, must of necessity produce different products on being alkylated.

α-Dimethylsafranine $C_{20}H_{19}N_4Cl$ is produced by the simultaneous oxidation of one molecule of paraphenylenedimethyldiamine with two molecules of aniline.

It is a dyestuff of a magenta-red shade. Its nitrate crystallises in green needles (Bindschedler, Ber. 16, 869).

β-Dimethylsafranine is obtained by oxidising a mixture of one molecule of paraphenylenediamine with one molecule of aniline and one molecule of dimethylaniline. Its shade is similar to that of the preceding one; its nitrate forms brown leaflets (Nietzki, Ber. 19, 3017 and 3136).

The two **diethylsafranines** are obtained in a similar manner. Their chlorides form green needles which dissolve in water with a violet

shade (Nietzki, Ber. 16, 464). These substances, and especially the α- derivatives, are manufactured under the name of *Fuchsia*.

Tetramethylsafranine (Bindschedler, *l.c.*) and **tetraethylsafranine** (Nietzki, *l.c.*) may be prepared by the joint oxidation of one molecule of paraphenylenedimethyl- (or diethyl-) diamine with one molecule of aniline and one molecule of dimethyl- or diethylaniline. These substances have been sold under the name of *Amethyst*. Their shade is a magnificent violet, with a fine crimson fluorescence. Unfortunately, they are very fugitive.

2. **Tolusafranines** (Hofmann and Geyger, Ber. 5, 526, and very numerous other publications) $C_{21}H_{21}N_4Cl$. A mixture of the isomerides of this formula is the safranine of commerce. It is prepared by the oxidation of a mixture of paratolylenediamine with the two toluidines. This mixture is obtained by treating three molecules of the orthotoluidine of commerce (which contains from 6 to 10 p.c. of paratoluidine) with two molecules of hydrochloric acid and one molecule of sodium nitrite dissolved in as little water as possible. A thick heavy oil is the result, which is merely a solution of amino-azotoluene in the excess of toluidine present. By dissolving this oil in hydrochloric acid, and reducing it with either zinc-dust or iron borings, the amino-azo- compound is split up into paratolylenediamine and orthotoluidine; consequently, the aqueous liquid produced contains the bases in the necessary proportions for the production of safranine. The rest of the treatment is exactly similar to the one described for pheno-safranine. The safranine is precipitated from the liquid by the addition of salt. By redissolving it in water, boiling with a small quantity of potassium bichromate, treating it afresh with milk of lime or chalk, and reprecipitating the filtered liquid with clean salt, the safranine is purified so as to give the brightest shades on dyeing. Safranine prepared with a toluidine rich in paratoluidine is very insoluble in cold water, and therefore generally disliked by the dyer. The presence of aniline has not the same disagreeable effect: some manufacturers therefore use the first runnings of the magenta process, which consist of aniline and orthotoluidine, and contain no paratoluidine, as a suitable raw product for the manufacture of safranine. The safranine of commerce forms a brown powder which dissolves readily in hot water. It dyes a bluish-pink on textile fibres, and was chiefly used for dyeing cotton. The introduction of the so-called substantive azo- colours, derived from benzidine and its congeners, has much diminished the use of safranine.

3. **Girofle.** A dimethylphenoxylosafranine has been produced by heating nitrosodimethylaniline hydrochloride with xylidine, and sold under the above name as a violet colouring matter of a pleasing shade.

4. **Safranisol** $C_{18}H_{13}(OCH_3)_2N_4Cl$ is a substance which has been obtained by Nietzki by the joint oxidation of one molecule of paraphenylenediamine with two molecules of orthoanisidine. It dyes a very beautiful yellowish-pink with a yellow fluorescence. This product has been patented (Kalle & Co., D. R. P. 24229), but owing to the high price of its production it has been unable to compete with the eosin colours, which are perhaps still more brilliant in shade.

5. **Magdala red** $C_{30}H_{21}N_4Cl$. This old and very beautiful colouring matter is the safranine of the naphthalene series. It was discovered by Schiendl and first investigated by Hofmann (Ber. 2, 374), who, however, owing to the great difficulties of its analysis, assigned to it the erroneous formula $C_{30}H_{21}N_3 \cdot HCl$. After a revision of the analytical data by Julius (Ber. 19, 1365), its true composition was established. This substance cannot be prepared by the usual oxidation process from paranaphthylenediamine and naphthylamine because paranaphthylenediamine is at once transformed into α-naphthaquinone even by the feeblest oxidising agents. Magdala red has therefore to be prepared by the old process of heating α-aminoazonaphthalene with α-naphthylamine acetate. The chief product of this reaction is rhodindine, the induline of the naphthalene series (*v.* INDULINES); but a small proportion (6–8 p.c.) of Magdala red is formed at the same time. This is extracted from the melt by repeated treatment with boiling water, in which it is sparingly soluble. On cooling, this solution deposits the dyestuff in the shape of gelatinous flakes, It is purified by repeated crystallisations from water. When pure, it forms a dark crystalline powder, which dissolves in alcohol with a pink colour and a magnificent orange fluorescence. It is used for dyeing light pinks on silk, but is now rapidly being replaced by rhodamine (*v.* TRIPHENYLMETHANE COLOURING MATTERS). If ready-formed paranaphthylenediamine be added to the magenta-melt, the proportion of Magdala red formed is considerably increased (Otto N. Witt, D. R. P. 40868). It is thus shown that Magdala red is, after all, only a product of the joint oxidation of paranaphthylenediamine and α-naphthylamine.

The pure salts of Magdala red, when recrystallised from spirit, form green needles with a metallic lustre. The chloride, sulphate, picrate, and platinum double chloride have been prepared and analysed. These salts dissolve in concentrated sulphuric acid with a blue-black colour which changes into red on dilution.

Mixed Magdala reds have been prepared either by heating amino-azonaphthalene with aromatic monoamines of the benzene series (M. T. Lecco, Ber. 7, 1290), or by heating aminoazo-compounds of the benzene series with paranaphthylenediamine hydrochloride and aniline, toluidine, or even phenol (Otto N. Witt, D. R. P. 40868). These dyestuffs resemble Magdala red in their properties.

6. **Indazine** is the commercial name of a safranine dye, which is obtained by heating the symmetrical diphenylmetaphenylenediamine (prepared by heating resorcin with aniline hydrochloride in the presence of zinc chloride) with nitrosodimethylaniline hydrochloride. Its constitution may be inferred from its analogy to the violet dyestuff prepared from nitrosodimethylaniline and phenyl-β-naphthylamine. It is a serviceable blue, of considerable intensity, but little brilliancy of shade.

Mauveine $C_{27}H_{25}N_4Cl$. This subtance, the oldest of all the artificial colouring matters, is still manufactured in a small way, and sold under

the name of rosolane. It was discovered and examined by W. H. Perkin (Roy. Soc. Proc. 35, 717), who also described the mode of its production. It is prepared by oxidising heavy aniline with potassium dichromate, and extracting the mauveïne formed with water or spirit from the black insoluble mass which is the chief product of the reaction. A dyestuff resembling mauveïne in all its properties may be prepared by the reaction of nitrosodiphenylamine on aniline (Otto Fischer and Hepp, Ber. 21, 2617) or by the joint oxidation of diphenylmetaphenylenediamine and paraphenylenediamine or metaaminodiphenylamine and para-aminodiphenylamine. These syntheses are a clue to the constitution of mauveïne, which has been a mystery for nearly half a century—it stands revealed as phenylphenosafranine. The above synthetical methods have been adopted for the industrial preparation of mauveïne, as they give better yields than Perkin's old process of oxidation. Mauveïne is generally sold in the shape of a violet paste. It is insoluble in cold, sparingly soluble in hot water, easily soluble with a fine purple shade in spirit. Concentrated sulphuric acid dissolves it with an olive-green colouration, which on dilution with water changes through green and blue into purple. Mauveïne still holds its own against the cheaper new violets on account of its great fastness to light and other influences. It is used for shading the white in bleached silks, and also for printing on paper.

Mauveïne yields on oxidation a pink dyestuff which is supposed to be identical with ordinary phenosafranine. In our opinion this statement requires confirmation. O. N. W.

AZOBENZENE $C_{12}H_{10}N_2$. A product of the partial reduction of nitrobenzene, obtained by Mitscherlich (Annalen, 12, 311) by boiling an alcoholic solution of nitrobenzene with potash and distilling the product.

Preparation.—Azobenzene is obtained by acting with sodium amalgam (4–5 p.c. of sodium) on nitrobenzene dissolved in ether containing water (Werigo, Annalen, 135, 176; Alexejeff, J. 1864, 525; Rasenack, Ber. 5, 367); the product, according to Alexejeff (J. 1867, 503) is azobenzene or azoxybenzene, according as the sodium amalgam or nitrobenzene is in excess. On the large scale azobenzene is prepared by the reduction of nitrobenzene in alcoholic solution with zinc-dust and aqueous soda. In this reaction the reduction tends to go further, and some hydrazobenzene is also obtained; this, however, is readily oxidised to azobenzene if nitrous fumes are passed into the alcoholic solution of the product (Alexejeff, J. 1867, 503). Azobenzene can also be prepared by distilling azoxybenzene (1 part) with iron filings (3 parts) (Schmidt and Schultz, Ber. 12, 484); by heating nitrobenzene on a water-bath with the calculated quantity (2 mols.) of stannous chloride dissolved in excess of aqueous caustic soda (Witt, Ber. 18, 2912); by reducing nitrobenzene in alcoholic solution with magnesium amalgam (yield 95 p.c.) (Evans and Fetsch, J. Amer. Chem. Soc. 1904, 1158); by reducing nitrobenzene with alkali sulphide in the presence of alkali (Farb. vorm. Meister, Lucius, and Brüning, D. R. P. 216246, J. Soc. Chem. Ind. 1909, 1310); by heating nitrobenzene with charcoal and alkali (Farb. vorm. Fried. Bayer & Co., D. R. P. 210806; Chem. Zentr. 1909, 2, 163); by treating phenylhydrazine with bleaching powder solution (Brunner and Pelet, Ber. 1897, 284). Azobenzene can be prepared by the electrolytic reduction of nitrobenzene in the presence of alkali (Elbs and Kopp, J. Soc. Chem. Ind. 1898, 1137; Löb, Ber. 1900, 2329; Farb. vorm. Fried. Bayer & Co., D. R. PP. 121899 and 121900; Chem. Zentr. 1901, 2, 153; Farb. vorm. Meister, Lucius and Brüning; D. R. P. 141535; Chem. Zentr. 1903, (i.) 1283; and Farb. vorm. Weiler-ter-Meer, D. R. P. 138496; Chem. Zentr. 1903, (i.) 372).

Properties.—Azobenzene crystallises in large yellowish-red crystals belonging to the monoclinic system (Boeris, R. Accad. Lincei, [5] 8, i. 575), and to the rhombic system (Alexejeff, Chem. Soc. Abstr. 42, 965); melts at 68°, boils at 293°, and is readily soluble in alcohol and ether, insoluble in water. From benzene it crystallises with benzene of crystallisation in rhombic prisms, which lose benzene on exposure to the air. Weak reducing agents, such as ammonium sulphide or zinc-dust in alkaline solution (Alexejeff, Annalen, 207, 327) or phenylhydrazine (Walther, J. pr. Chem. 1896, 54, 433), convert azobenzene into hydrazobenzene, but benzidine is obtained when stronger reducing agents such as sulphurous acid or hydrogen iodide are employed (Bordenstein, D. R. P. 172569; J. Soc. Chem. Ind. 1907, 272), or the alcoholic solution is treated in the cold with stannous chloride and a little sulphuric acid (Schultz, Ber. 17, 464; Mentha and Heumann, Ber. 19, 2970). Azobenzene can also be electrolytically reduced to benzidine (Löb, Ber. 1900, 2329; when heated with ammonium hydrogen sulphite and alcohol under pressure, it is converted into benzidinesulphamic acid (Spiegel, Ber. 18, 1481). When melted with *p*-phenylenediamine in the presence of ammonium chloride, it yields a soluble induline dye (Farb. vorm. Fried. Bayer & Co., D. R. P. 53198; Ber. 1891, Ref. 137). Azobenzene yields a mixture of mono-, di-, and trinitroazobenzenes when treated with fuming nitric acid (Gerhardt and Laurent, Annalen, 75, 73; Janovsky and Erb, Ber. 18, 1133; 19, 2157; Janovsky, Monatsh. 7, 124; Werner and Stiasny, Ber. 1899, 3256): ordinary sulphuric acid dissolves it without alteration, whilst the fuming acid at 130° converts it into azobenzenemonosulphonic acid (Griess, Annalen, 154, 208; Janovsky, Monatsh. 2, 219); chromic acid oxidises it to carbon dioxide and nitrogen (De Coninck, Compt. rend. 1899, 128, 682). The bromine derivatives of azobenzene have been examined by Werigo (Annalen, 165, 189), Janovsky (*l.c.*), and Mills (Chem. Soc. Trans. 1894, 51).

AZOBENZENE RED *v.* AZO- COLOURING MATTERS.

AZO-BLACK or **NAPHTHOL BLACK** *v.* AZO- COLOURING MATTERS.

AZO-BLUE *v.* AZO- COLOURING MATTERS.

AZO-COCCINE *v.* AZO- COLOURING MATTERS.

AZO- COLOURING MATTERS.

History.—The colouring matters of this class contain one or more azo- groups—N : N—linking together aromatic radicles. The typical parent substance from which these compounds may be regarded as being derived is azobenzene

$C_6H_5{\cdot}N:N{\cdot}C_6H_5$, which has been known since the year 1834 (Mitscherlich, *Annalen*, 12, 311). The basic and acid derivatives of azobenzene are all colouring matters, the amino- derivative, aminoazobenzene, having been the first of these compounds which was prepared and introduced into commerce on anything approaching a large scale by the firm of Simpson, Maule, and Nicholson in 1863. This substance was prepared by the action of nitrous gases on aniline dissolved in alcohol, and was known in the market by the name of 'aniline yellow,' the true constitution of the colour being at the time unknown. The introduction of the first azo-colour into commerce is thus due to the firm above mentioned, although the production of the colour itself appears to have been previously observed by Mène (Compt. rend. 1861, 52, 311), Luthringer (Brevet d'invention, Aug. 30, 1861), and Griess (Annalen, 1862, 121, 262, *note*). The first researches on the diazo- compounds (as distinguished from azo- compounds) were published in 1858 by Griess (Annalen, 106, 123), who in 1862 discovered a compound produced by the action of nitrous acid on aniline, to which he gave the name of 'diazoamidobenzol' (Annalen, 131, 257). The latter was, however, a true diazo- compound, and on comparing it with the 'aniline yellow' of commerce it was found that the two substances were isomeric, a discovery which led to the establishment of the true formula of aminoazobenzene by Martius and Griess in 1866 (Zeitsch. Chem. N. F. 2, 132). In this same year a brown dye was sent into the market by the firm of Roberts, Dale, and Co., of Manchester, and this colouring matter (known as Manchester Brown, Vesuvine, Phenylene Brown, or, more generally, Bismarck Brown) was investigated by Caro and Griess, and identified as an azo- compound in 1867 (Zeitsch. Chem. N. F. 3, 278). These chemists regarded it as triaminoazobenzene, but G. Schultz (Chemie des Steinkohlentheers, 2nd ed. 2, 193) showed that it is benzene-1 : 3-disazophenylenediamine. This compound still occupies an important place in the tinctorial industries, whilst the earlier known aminoazobenzene (aniline yellow) has been completely abandoned on account of its fugitive character. It is, however, used in the preparation of other azo-colouring matters and indulines. In 1876 a beautifully crystalline orange colouring matter made its appearance as a commercial product under the name of 'chrysoïdine,' its composition and constitution having been established by Hofmann (Ber. 1877, 10, 213), who showed that it was diaminoazobenzene. This colouring matter was discovered almost simultaneously by Caro and Witt, independently, in 1876, but was first introduced into commerce by the latter, the manufacture having been carried out by the firm of Williams, Thomas, and Dower, of Brentford and Fulham.

The manufacture of chrysoïdine was the first industrial application of Griess's discovery of the diazo- compounds, the colouring matter in question being prepared by the action of a diazo-salt (diazobenzene chloride) on *m*-phenylenediamine, and this manufacture was soon followed by the appearance of acid azo- compounds prepared by the action of diazosulphonic acids on phenols. The typical parent substance of these acid azo- colours may be regarded as hydroxyazobenzene, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, which was first prepared by Griess in 1864 (Phil. Trans. 153, 679). The general method by which the azo- colours are now prepared is an application of the reaction between diazo- salts and phenols in alkaline solution, first made known by Kekulé and Hidegh (Ber. 1870, 3, 233), the first colouring matters of this class having been introduced by Witt under the name of 'Tropæolines' (Chem. Soc. Trans. 1879, 35, 179), and simultaneously by Poirrier, of St. Denis, under the designation of 'Orange' of various brands. Since the first appearance of the acid azo- colours immense numbers of these compounds have been sent into commerce under various designations, the first patent having been taken out by Griess in 1877 (E. P. 3698), and being quickly followed by others, which will be referred to in due order. Of the acid azo- colours described in the earlier specifications, the most successful from an industrial point of view were those manufactured by the 'Badische Anilin- und Soda-Fabrik' (Ber. 1879, 12, 1364), and by Meister, Lucius, und Brüning, of Höchst (*ibid.* 144).

The next step of importance in the industrial history of the azo- colours was the introduction of *disazo- compounds*, containing two azo- groups. The typical compound of this class is benzeneazobenzeneazophenol $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, discovered in 1877 by Caro and Schraube (Ber. 10, 2230). In 1879 appeared the 'Biebrich scarlet' of Nietzki (Ber. 1880, 13, 800, 1838), which was introduced by the firm of Kalle & Co. of Biebrich. This dyestuff is prepared by combining diazotised aminoazobenzenedisulphonic acid with β-naphthol, and was the first of the *secondary* disazo- compounds. The first *primary* disazo- colouring matter, 'Resorcin brown,' was discovered in 1881 by Wallach, who combined *two* molecules of a diazo- compound (*m*-xylidine and sulphanilic acid) with *one* molecule of a phenol (resorcinol). In 1884 a very important discovery in the history of azo-colouring matters was made by P. Böttiger, who found that the disazo- compound obtained by combining the tetrazo- salt prepared from benzidine with naphthionic acid possessed the valuable property of dyeing cotton direct, without the use of a mordant. This colouring matter was put on the market by the Aktiengesellschaft für Anilinfabrikation, under the name of 'Congo red.' This discovery has given rise to the production of a very large number of similarly constituted colouring matters, which appear on the market under the names of benzo-, Congo-, diamine-, and other dyestuffs. In the following year another important development was announced by the introduction of the first satisfactory black azo- colouring matter (naphthol black) for wool. This was discovered by Hoffmann and Weinberg, and placed on the market by L. Cassella & Co. In 1887 A. G. Green found that primuline, which he had discovered, dyed cotton direct, and that the yellow colouring matter when thus dyed on the fibre, could be diazotised and combined (developed) with β-naphthol, *m*-phenylenediamine, and similar 'developers,' thus giving rise to a series of new azo- dyestuffs (Ingrain colours). This discovery led to the manufacture of many azo-colouring matters which were capable of being

similarly diazotised and developed on the fibre (*e.g.* diamine black), as also to the production of azo- colouring matters on the fibre by treating the fibre already dyed with an azo- colour with a diazo- compound (*e.g.* benzonitrol colours). In both cases darker and faster dyeings are obtained.

The first direct cotton black (diamine black, RO) was discovered in 1889 by Gans (Cassella & Co.), and in 1891 Hoffmann and Daimler prepared the first green colouring matter of this kind (diamine green).

A modified method of the process introduced in 1880 by Read Holliday and Sons, of producing insoluble azo- colouring matters directly on the fibre, has been largely developed of late years. The first example of this, viz. the combination of diazotised *p*-nitroaniline with *β*-naphthol (' paranitraniline red ') still holds the place of greatest importance.

Manufacture.—The general method of preparing the azo- colours on a large scale depends upon the reaction between a diazo- salt, usually the chloride, and a phenol or phenolsulphonic acid in presence of an alkali, as typified by the following example :—

$$\underset{\text{Diazobenzene chloride.}}{C_6H_5\cdot N_2Cl} + \underset{\text{Sodium phenoxide.}}{C_6H_5\cdot ONa} = \underset{\text{Benzeneazophenol.}}{C_6H_5\cdot N_2\cdot C_6H_4\cdot OH} + NaCl.$$

Aminosulphonic acids or aminocarboxylic acids when diazotised react in a similar manner :

$$\underset{\text{Diazosulphanilic acid.}}{C_6H_4\langle^{N_2}_{SO_3}\rangle} + \underset{\text{Sodium phenoxide.}}{C_6H_5\cdot ONa} = \underset{\text{Sulphobenzeneazophenol (sodium salt).}}{SO_3Na\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot OH}.$$

Preparation of the diazo- salts.—The amine to be diazotised is usually dissolved in about 10 parts of water and one equivalent of hydrochloric (more rarely sulphuric) acid. For diamines twice this amount of acid is taken. The solution[1] is now cooled by adding ice until the temperature is, in the case of aniline, the toluidines, the xylidines, &c., 0°–2°, or, in the case of the naphthylamines, the nitroanilines and diamines such as benzidine, tolidine, dianisidine, &c., 5°–10°. This is done by adding ice to the solution. More acid (1½–2 equivalents) is now added (or 3–4 in the case of diamines), and a solution of the calculated quantity of sodium nitrite is run in, sufficient being used to give a reaction with starch-iodide paper after the whole has been mixed for two or three minutes. (For velocity of diazotisation, *see* Hantzsch and Schumann, Ber. 1899, 32, 1691; Schumann, *ibid.* 1900, 33, 527.) In certain cases (*e.g.* α-naphthylamine, *p*-nitroaniline, &c.) it is better to add the nitrite all at once in order to avoid the formation of the diazoamino- compound. In diazotising such compounds as give an insoluble diazo- derivative, as, for example, *p*-sulphobenzeneazo-α-naphthylamine or *p*-acetylaminobenzeneazo-α-naphthylamine, and which themselves are insoluble in acids (under the above conditions) it is advisable to use an excess of nitrite and to stir the ice-cold mixture for several hours. Special methods have to be employed to diazotise amines containing several negative groups; the operation may often be effected by carrying it out in the presence of excess of 50 p.c. sulphuric acid, and Witt has shown (Ber. 1909, 42, 2953) that diazotisation is easily brought about in these cases by employing strong nitric acid. Other substances which are difficult to diazotise satisfactorily are those which are readily oxidised by the nitrous acid, such as the 1 : 2- and the 2 : 1-aminonaphthols and their sulphonic acids. In this case the diazotisation may be done in the presence of zinc or copper salts (compare E. P. 10235 of 1904; D. R. P. 171024, 172446; E. P. 353786) or by means of zinc nitrite. Another method is to diazotise in presence of an excess of acetic or oxalic acid (compare D. R. P. 155083, 175593, also E. P. 2946 of 1896).

Difficulties are often encountered in endeavouring to diazotise certain diamines. *o*-Phenylene- and tolylene-diamines cannot be diazotised, as they yield the azimino- derivatives, and, under the usual conditions, the meta-diamines furnish Bismarck brown; but if the diamine is run into a mixture of nitrite and acid the tetrazo- compound may be obtained (Griess, Ber. 1886, 19, 317; Täuber and Walder, Ber. 1897, 30, 2901; E. P. 1593 of 1888; D. R. P. 103685). In the case of *p*-phenylenediamine and certain diamines of the naphthalene series diazotisation is brought about indirectly, as the direct action of nitrous acid often leads to a mixture of the mono- with the bis-diazo- (or tetrazo-) compound. Either the corresponding nitroamine or the monoacetylated diamine is employed. This is diazotised and combined with a component in the usual way (*see* below), and then the nitro- group is reduced or the acetyl group hydrolysed when the free amino- group can then readily be diazotised. Some diamines, indeed, can only be diazotised as regards one amino- group, the other being quite unattacked. In such cases (*e.g.* *o*-nitro-*p*-phenylenediamine, 1 : 4-naphthylenediamine-2-sulphonic acid—the latter being diazotisable only in acetic or oxalic acid solution) the monodiazo-salt is combined with a component and then the remaining amino- group, which before resisted all attempts at diazotisation, is easily diazotised (compare Bülow, Ber. 1896 29, 2285; E. P. 2946 of 1896). (For further information on this subject, see Cain, The Chemistry of the Diazo- Compounds, Arnold, 1908.)

Combination (coupling) of the diazo- compound with a component (phenol or amine) to form an azo- dyestuff.—Before the diazo- solution is prepared a solution of a phenol or amine is made ready so that no delay may occur before coupling takes place. As a general rule, phenols are combined in alkaline and amines in acid (acetic) solution. In the case of phenols or naphthols the substance is first dissolved in the calculated amount of sodium hydroxide, the solution diluted with water, and sodium carbonate added in sufficient quantity to ensure an alkaline reaction being obtained at the end of the combination (*i.e.* a little more than one molecule of sodium carbonate to each molecule of hydrochloric acid, so that sodium hydrogen carbonate may be formed). When phenolic sulphonic acids

[1] Some of the diazosulphonic acids, such as diazonaphthionic acid, are insoluble in water, and are therefore employed in a state of suspension.

are the components, they may be dissolved in sodium carbonate instead of hydroxide. The phenolic solution, having been cooled to about 10°, is now ready, and the diazo- solution is run in gradually with constant stirring. Combination takes place at once,[1] and when all the diazo- solution has been added, the mixture must be tested to ensure an alkaline reaction, and the presence of a slight excess of the phenol (about 2–5 p.c. excess of the theoretical amount is usually taken). The next day the colouring matter is filtered through filter presses. If it has separated out, no further treatment is necessary, but if it is still partly or wholly in solution, it is 'salted out' (hot or cold) by adding common salt until a spot on filter paper shows only a faintly coloured rim. In rare cases the precipitation is effected by acidifying. The filtration is best effected by the aid of compressed air and the press cake is spread on trays and dried. The dry lumps are then ground in a mill, adjusted to 'type' or 'standard' by means of common salt, sodium sulphate, &c., and the product is then ready for the market. In cases where the possibility of the formation of a disazo- dyestuff is present (dihydroxy- compounds, α-naphthol, &c.), the coupling may advantageously be carried out in acetic acid solution.

The procedure adopted in the case of amines is very similar to the above. The amine is first dissolved in the appropriate amount of hydrochloric acid, the solution diluted and sufficient sodium acetate added to ensure that no free mineral acid remains at the end of the combination (in rare cases coupling is effected in mineral acid or alkaline solution). When the combination is complete, the dyestuff is filtered off either as it is or after having been rendered alkaline.

Many disazo- dyestuffs are prepared by combining two molecules of the same or different diazo- compounds with an aminonaphtholsulphonic acid. In this case combination is effected first in acid solution and then the monoazo- dyestuff thus formed is rendered alkaline, and the second molecule of diazo- compound added.

Position assumed by the azo- group in the formation of azo- colouring matters.—(*a*) *Benzene series*: When the para- position with respect to the amino- or hydroxy- group is occupied by a hydrogen atom, and no group, such as NO_2, SO_3H, or NR_3Cl, is in the meta- position, the azo- group enters the para- position in place of the hydrogen atom. (*b*) *Naphthalene series*: In corresponding compounds of the naphthalene series (α-naphthylamine, α-naphthol) the entering azo- group also takes up the para- position, but when, in α-naphthol, a sulphonic group is in the 3- or 5-position with respect to the hydroxy- group, or a nitro- or NR_3Cl- group is in the 3- position, the azo- group enters the 2- position.

When the para- position is substituted, the azo- group enters the ortho-(2)- position, but if the para- substituent is a carboxy- group, this is usually displaced by the azo- group.

When diazo- compounds act on β-naphthylamine or β-naphthol, the azo- group enters position 1 (in the ortho- position with respect to the amino- or hydroxy- group). If the 1- position in β-naphthol is occupied by a carboxy- group, this is displaced (compare also Scharwin and Kaljanoff, Ber. 1908, 41, 2056 and article on DISAZO- and TETRAZO- COLOURING MATTERS).

Differing capacity for combination.—As will have been gathered from the preceding paragraph, the azo- group never enters the meta- position with respect to an amino- or hydroxy- group. Further, a component in which the para- position is occupied by a substituent group is not so readily attacked (in the ortho- position) as one that is not substituted (when the azo- group enters the para- position). Moreover, the capacity for combination depends also on the kind of diazo- compound employed, thus 2-naphthol-8-sulphonic acid and 2-naphthol-6 : 8-disulphonic acid in dilute solution do not combine at all with diazotised xylidine or naphthylamine, whilst diazotised aniline, aminoazobenzene, aminoazobenzenesulphonic acid and naphthylaminesulphonic acids couple easily with them. The combination with diazotised xylidine and naphthylamine can, however, be made to take place in concentrated solution. The diazo- compound of *p*-nitroaniline, in most cases, combines with extreme ease. Finally, 2-naphthylamine-6 : 8-disulphonic acid does not combine with any diazo- compound. (For measurement of the rate of formation of dyestuffs, *see* Goldschmidt, Ber. 1897, 30, 670, 2075; 1899, 32, 355; 1900, 33, 893; 1902, 35, 3534; Veley, Trans. Chem. Soc. 1909, 95, 1186.)

Considering now the formation of azo- dyestuffs from tetrazotised diamines, it should be noted that diamines of the type of benzidine furnish tetrazo- compounds which can either be combined with two molecules of one component (phenol or amine) or with one molecule each of two components, and the reaction can thus be divided into two stages. This holds good even when one component only is used; thus tetrazotised benzidine combines almost at once with one molecule of naphthionic acid, forming a so-called intermediate product; but the second molecule of naphthionic acid combines with this only slowly. Here also a difference in combining power is to be noted, thus tetrazotised benzidine combines more readily than does the corresponding compound from tolidine.

General properties.—(1) *Action of alkalis.* Hydroxyazo- dyes containing a sulphonic or carboxylic group usually form differently coloured salts, and consequently the addition of sodium hydroxide to their solutions produces a modification in the shade (compare Hewitt and Mitchell, Trans. 1907, 91, 1251). The isomeric colouring matters prepared from α- and β-naphthol show a characteristic difference in that only those derived from the former are changed by sodium hydroxide (*e.g.* benzoazurine, &c.).

(2) *Action of cold dilute acids.* Dyestuffs containing amino- or substituted amino- groups generally undergo a change when treated with dilute acid (compare Fox and Hewitt, Trans. 1908, 93, 333; Hewitt and Thomas, *ibid.* 1909, 95, 1292; Hewitt and Thole, *ibid.* 1909, 95, 1393; 1910, 97, 511). In the case of Congo

[1] For the formation of diazo-oxy- compounds, *see* a paper by Dimroth and Hartmann, Ber. 1908, 41, 4012.

red and methyl orange this change is so profound that these colouring matters can be used as indicators.

(3) *Action of cold concentrated sulphuric acid.* Nearly all azo- colouring matters give characteristic colour changes with this reagent, and it is often used as an aid in the detection of dyes. Mixtures of dyes, when covered with sulphuric acid, often reveal themselves by the various colours produced by the particles as they become dissolved. There are certain relationships between the colour of the solution of azo- dyes in sulphuric acid, and therefore of their absorption spectra and their chemical constitution. Thus the dyestuff from aminoazobenzenesulphonic acid and β-naphthol gives a green colour, those from the same (diazotised) amine and β-naphtholsulphonic acids, a blue, and those from aminoazobenzene and its homologues combined with β-naphtholsulphonic acids a red violet (compare Ber. 1880, 13, 1840; Vogel, Sitzungsber. K. Akad. Berlin, 1887, 34, 715; Ber. 1889, 22, 634, 2062; Schütze, Zeitsch. physikal. Chem. 1892, 9, 2; Grebe, Diss. Leipzig, 1892).

(4) *Action of hot hydrochloric acid.* Certain azo- colouring matters, such as, for example, aminoazobenzene, are decomposed when boiled with concentrated hydrochloric acid; reduction and oxidation take place accompanied by chlorination. In the instance quoted phenylenediamine, aniline, and benzoquinone or its chloro- derivatives are produced (Wallach and Kölliker, Ber. 1884, 17, 395).

(5) *Action of hot sulphuric acid* (Witt, Ber. 1887, 20, 571). Azo- colouring matters which are derived from phenyl- or tolyl-β-naphthylamine by the action of diazo- compounds on these bases, when boiled with moderately dilute sulphuric acid, yield the bases, or their sulphonic acids, from which the diazo- compound was prepared, together with naphthazines. Thus the dyestuff obtained by combining diazotised sulphanilic acid with phenyl-β-naphthylamine, is decomposed into sulphanilic acid and phenonaphthazine:

$$SO_3H\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_6H_5$$

$$=SO_3H\cdot C_6H_4\cdot NH_2+C_{10}H_6\begin{array}{l}N\\|\\N\end{array}C_6H_4.$$

(6) *Action of nitric acid.* Azo- colouring matters are readily attacked by nitric acid, and the course of the reaction depends largely on the conditions of temperature and concentration. By the moderate action of nitric acid, the dyestuff may simply be nitrated, thus diphenylamine orange yields curcumeine and, by further action, azo- acid yellow, the dyestuffs in both cases, however, being accompanied by some nitrodiphenylamine produced by the fission of the azo- group. Also when flavazol (diazotised toluidine combined with salicylic acid) is nitrated, it yields Persian yellow (*o*-nitrotoueneazosalicylic acid) (compare Ber. 1906, 40, 4207).

Methyl orange is decomposed even by cold dilute nitric acid; a methyl group is eliminated in the process, and dinitromonomethylaniline is produced. The presence of a diazo- compound can also be detected (Fox, Ber. 1908, 41, 1989).

Cold fuming nitric acid decomposes many azo- colouring matters (particularly those containing an amino- or hydroxy- group in the para- position with respect to the azo- group), with the production of the diazo- compound from which the dye is prepared and the nitro- derivative of the other component; thus, orange II yields diazotised sulphanilic acid, and a nitro- derivative of β-naphthol and methyl orange gives *op*-dinitrodimethylaniline, tetranitrodimethylaniline and diazotised sulphanilic acid (O. Schmidt, Ber. 1905, 38, 3201).

Finally, warm nitric acid usually decomposes azo- dyestuffs, with the production of nitrophenols or bases.

(7) *Action of chlorine and bromine.* All azo- colouring matters are readily attacked by chlorine or bromine. Fission generally takes place at the azo- group with the production of halogenated phenols, but some dyestuffs are converted into substitution products (compare Ber. 1884, 17, 272).

(8) *Action of reducing agents.* Reducing agents, such as zinc-dust and water, zinc-dust and ammonia, or sodium hydroxide, zinc-dust and dilute acids, tin and hydrochloric acid, stannous chloride and sodium hyposulphite (technically known as 'hydrosulphite') (Grandmougin, Ber. 1906, 39, 2494, 3561, 3929; compare also J. pr. Chem. 1907, (ii.) 76, 124; Franzen and Stieldorf, J. pr. Chem. 1907, (ii.) 76, 467; O. Fischer, Fritzen and Eilles, J. pr. Chem. 1909, (ii.) 79, 562) attack the azo- group and convert it into two amino- groups; thus:

$$NH_2\cdot C_6H_4\cdot N:N\cdot C_6H_5+2H_2$$
$$=NH_2\cdot C_6H_4\cdot NH_2+C_6H_5\cdot NH_2.$$

The base which was used to provide the diazo- compound is thus regenerated, whilst the other component is converted into its amino- derivative.

By careful reduction with zinc-dust, dyestuffs obtained by the combination of diazotised aminoazobenzenesulphonic acid with phenols yield the aminoazosulphonic acid without the latter undergoing reduction. Further, nitroazo- dyestuffs can be reduced to the corresponding aminoazo- dyestuffs with sodium sulphide. The reduction of azo- dyestuffs is a useful means of attacking the problem of their constitution, although the operation requires considerable care (compare Witt, Ber. 1886, 19, 1719; 1888, 21, 3468, and especially the references quoted in connection with reduction by hydrosulphite).

Azo- dyestuffs are also readily reduced by titanous chloride, and a process for their estimation by titration with this reagent has been worked out by Knecht (J. Soc. Dyers, 1903, 19, 169; Ber. 1903, 36, 166, 1549; 1907, 40, 3819). A detailed account of the method of carrying out this and other methods of reduction will be found in Hans Meyer's Analyse und Konstitutionsermittelung organische Verbindungen, 2te aufl. 1909, p. 870.

(9) *Identification of azo- colouring matters on the fibre.* This is carried out by observing the action on the dyed fabric of various reagents, for which various tables have been constructed (compare Cain and Thorpe, The Synthetic Dyestuffs, 1905; Lunge, Chemisch-technische Untersuchungensmethoden, Eng. trans., edited by Keane, 1911).

Direct formation of azo- colours in the fibre.— The production of an insoluble azo- dyestuff in

the fibre was first achieved by T. and R. Holliday (E. P. 2757 of 1880), who impregnated the fibre with α- or β-naphthol, passed it then through a diazo- solution, and finally developed the colour by treatment with alkali. An improvement on this process was introduced by the Farbwerke vormals Meister, Lucius und Brüning, in 1889, which consisted in 'padding' the fibre (generally cotton) with the sodium salt of a phenol (usually β-naphthol), and passing the cloth through a diazo- solution, the free mineral acid of which has been neutralised by adding sodium acetate. This process is very largely used at the present day, and is applied to the greatest extent to the production of the so-called 'para-red' (the azo- colour obtained by combining diazotised *p*-nitroaniline with β-naphthol). The colouring matters produced in this way will now be described.

Paranitraniline Red. The colouring matter was first prepared in substance by Meldola (Chem. Soc. Trans. 1885, 47, 657) by combining diazotised *p*-nitroaniline with β-naphthol in alkaline solution. As stated above, it is now almost entirely produced on the fibre. The goods are soaked in a bath containing sodium β-naphthoxide and Turkey-red oil, or thickening materials, squeezed out and dried at 65°–80°. They are then passed through the diazo- solution, washed and soaped. In order to avoid preparing the diazo- solution in the dye-house, various preparations may be used. Thus, **Paranitraniline extra N** paste is a mixture of *p*-nitroaniline with the calculated amount of sodium nitrite, and needs only to be stirred slowly into the necessary quantity of hydrochloric or sulphuric acid, ice, and water, to produce the diazo- solution. A similar product is **Benzonitrol** paste. Other preparations contain the diazo- compound in a suitable form for keeping. Thus, **Nitrosamine Red** is the sodium salt of *p*-nitro*anti*diazobenzene (which is very stable) and furnishes the true diazo- solution when mixed with dilute acid. **Azophor Red, Azogen Red** and **Nitrazol C**, are mixtures of the diazo- sulphate with sodium sulphate (whereby sodium hydrogen sulphate is produced); they are dissolved in water, the solution filtered, if necessary, and neutralised before use with sodium acetate or hydroxide. Paranitraniline red is used as a substitute for the red Congo dyestuffs and for Turkey red. It is extracted from the fibre when treated with organic solvents, and when the fibre is heated to 180°–200° the dyestuff partly sublimes. (For the formation of paranitraniline red, *see* Pomeranz, Zeitsch. Farben. Ind. 1906, 5, 184; Erban and Mebus, Chem. Zeit. 1907, 31, 663, 678, 687; Lichtenstein, Zeitsch. Elektrochem. 1908, 14, 586; Prud'homme and Colin, Rev. Gen. Mat. Col. 1909, 13, 1, 66; Bull. Soc. chim. 1909, (iv.) 5, 779; Bucherer, and Wolff, Zeitsch. angew. Chem. 1909, 22, 731; Justin-Mueller, Bull. Soc. chim. 1910, (iv.) 7, 60.)

Metanitraniline Orange and **Nitro-*o*-toluidine Orange.** Prepared as above from diazotised *m*-nitroaniline or nitro-*o*-toluidine and β-naphthol. The former gives yellowish and the latter reddish shades of orange. Their use is not very extensive, as they are not fast to rubbing, and the colours sublime on keeping. An orange free from these disadvantages can, however, be obtained by using *m*-nitro-*p*-phenetidine.

Nitrophenetidine Rose or **Blue-red.** Here *o*-nitro-*p*-phenetidine is used as the diazotised base. A substitute for this is **Azophor Rose A**, which is a mixture of a 'stable' diazo- compound with β-naphthol. Other rose shades are produced by the use of *p*-nitro-*o*-anisidine.

Naphthylamine Bordeaux. Prepared on the fibre from diazotised α-naphthylamine and β-naphthol. The dyestuff is used also as a pigment colour under the names **Carminaph Garnet** (D. H.[1]) and **Cerotine Scarlet 2 R** (C. J.).

Azo Turkey Red is produced by treating cloth padded with β-naphthol with diazotised β-naphthylamine. It is a bright scarlet, which, however, is not very fast.

Fast Azo Garnet. Prepared from diazotised *o*-aminoazotoluene and β-naphthol. It is also manufactured in substance and is used for colouring oils and varnishes under the names **Oil Scarlet** (M) (K) (W), **Red B, Oil soluble, extra conc.** (Remy), **Cerotine Ponceau 3 B** (C. J.), and **Fat Ponceau R** (K).

Benzidine and Tolidine Puce. Obtained from tetrazotised benzidine or tolidine and β-naphthol. Dark garnet to brown shades are produced which, however, are not fast to light. Rather yellower shades result by using tetrazotised diaminocarbazole instead of these diamines; when treated with copper salts the tints are very fast to light.

Dianisidine Blue. Tetrazotised dianisidine is combined on the fibre with β-naphthol in presence of copper salts. The tetrazo-compound is also put on the market as **Azophor Blue D**, a mixture of the tetrazo- compound and aluminium sulphate which has been dried in a vacuum at 45°. The colour is very fast to light, soap, and rubbing.

The production of black insoluble colours in the fibre was first effected by the Farbwerke vorm. Meister, Lucius und Brüning. The cloth is padded with β-naphthol and tragacanth, and treated with a mixture of the tetrazo-compounds of dianisidine and certain other bases. The mixture of bases sold for this purpose is known as **Azo Black Base O**, and the diazo- compounds are put on the market under the name of **Azophor Black S.** Cassella & Co. have introduced a black obtained by padding the cloth with 1 : 6- or 1 : 7-aminonaphthol, and then passing it through diazotised *p*-nitroaniline so as to form the disazo- colouring matter. The aminonaphthol is put on the market as **Amidonaphthol BD** and **3 B**, and both brands are mixtures of the two aminonaphthols mentioned. Full black colours are obtained which are fast to soap and chlorine, but they are not very easily applied in printing. A black, also introduced by the same firm, is produced from **Azotol C**, which is an asymmetric dialkylated di-*p*-diaminoazobenzene (it is identical with Kinzlberger's **Ice Black**). The base is diazotised and combined with β-naphthol on the fibre in the usual way. The latter firm also has introduced the use of the diazo- compound of aminochrysoïdine, and of the tetrazo- compound of *pp*-diaminodiphenylamine for the production of black colours. Other tetrazo-compounds recommended are these of aminobenzene-azo-α-naphthylamine (By.) and diaminodimethylcarbazole (M.).

[1] See p. 364 for the full names of firms of which these letters are a contraction.

Another process of producing azo- colouring matters on the fibre is by the use of primuline (*q.v.*). When cotton dyed with this dyestuff is treated with a solution containing hydrochloric acid and sodium nitrite, the dyestuff is diazotised. The cloth is now passed through a bath containing the 'developer,' consisting of a solution of an amine or a phenol. β-naphthol is mostly used in giving **Ingrain-** or **Primuline Red.** An orange colour is obtained with resorcinol (**Ingrain Orange**), and a brown with *m*-phenylenediamine (**Ingrain Brown**). Many direct-dyeing cotton colours which contain a diazotisable amino- group (for example, diamine black BH) acquire a faster, deeper, and modified shade when similarly diazotised on the fibre and developed with β-naphthol or *m*-phenylenediamine.

In the succeeding portion of this article it is proposed to give an account of the most important azo- colours which are at present in commerce.[1] Each colour will be treated of under its commercial name; its chemical formula given, and the mode of preparation and general properties briefly described.

Unless otherwise stated, it may be assumed that colouring matters containing a sulphonic or carboxylic group are placed on the market in the form of their sodium salts.

The following abbreviations are used for the names of firms:—

(A.) = Aktiengesellschaft für Anilinfabrikation, Berlin.
(B.) = Badische Anilin- und Soda-Fabrik, Ludwigshafen a/Rhein.
(Bl.) = The Basle Chemical Company.
(By.) = Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld.
(C.) = Leopold Cassella & Co., Frankfurt a/Main.
(C. J.) = Carl Jäger, G. m. b. H., Düsseldorf-Derendorf.
(Cl. Co.) = The Clayton Aniline Co., Ltd., Clayton, Manchester.
(Claus & Co.) = Claus & Co., Clayton, Manchester.
(D.) = Dahl & Co., Barmen.
(D. H.) = Dye Works, formerly L. Durand, Huguenin, & Co., Basle.
(F.) = A. Fischesser & Co., Lutterbach.
(G.) = Aniline Colour- and Extract-Works, formerly John R. Geigy, Basle.
(H.) = Read Holliday and Sons, Ltd., Huddersfield.
(I.) = Société pour l'Industrie Chimique, (formerly Bindschedler und Busch), Basle.
(K.) = Kalle & Co., Biebrich a/Rhein.
(K. S.) = Sandoz & Co. (formerly Kern and Sandoz), Basle.
(L.) = Farbwerk Mülheim (formerly A. Leonhardt & Co.), Mülheim, near Frankfurt.
(Lev.) = Levinstein, Ltd., Blackley, Manchester.
(M.) = Farbwerke vorm. Meister, Lucius, und Brüning, Höchst a/Main.
(N. I.) = Farbwerk Griesheim, Nötzel, Istel & Co., Griesheim a/Main.
(O.) = Chemische Fabrik Griesheim-Elektron, Werk Oehler (formerly K. Oehler), Griesheim.
(P.) = Société Anonyme des Matières Colorantes & Produits Chimiques de St. Denis, Paris.
(P. L.) = Pick, Lange & Co., Amsterdam.
(Sch.) = The Schöllkopf Aniline and Chemical Company, Buffalo, U.S.A.
(T. M.) = Chemische Fabriken vorm. Weiler ter Meer, Uerdingen a/Rhein.
(W.) = Williams Bros. & Co., Hounslow, Middlesex.

Also E. P. = English Patent; D. R. P. = German Patent; F. P. = French Patent; A. P. = American Patent.

[1] **Wool Scarlet R** (Sch.), **Croceine 3 B** (Sch.), and **Diamine Red NO** (C.) are no longer manufactured, according to information received by the writer from the manufacturers indicated. Since the firm Brooke, Simpson, and Spiller, Ltd., ceased to exist, some of the colouring matters made by them are now manufactured by Messrs. Claus and Co., of Manchester.

I. Basic Azo- Compounds.

Aniline Yellow; Aminoazobenzene

$$C_6H_5\cdot\overset{[1]}{N_2}\cdot C_6H_4\cdot\overset{[4]}{NH_2}.$$

This compound, discovered by Mène in 1861 (Jahresber. p. 496), and introduced into commerce by Simpson, Maule, and Nicholson in 1863, is interesting as being the first azo- colour made on a manufacturing scale. It was formerly prepared by passing nitrous acid gas into an alcoholic solution of aniline. As a colouring matter it is now of no importance, but is largely used as the starting-point in the manufacture of other azo- colours and of indulines. In practice this compound cannot be prepared directly by the action of one molecule of nitrous acid on two molecules of aniline, since diazoaminobenzene is always the first product of this reaction:

$$2C_6H_5\cdot NH_2,HCl+NaNO_2 = C_6H_5\cdot N_2\cdot NH\cdot C_6H_5+NaCl+HCl+2H_2O.$$

The diazo- compound is slowly converted into the isomeric aniline yellow on being kept for some time in contact with aniline and an aniline salt:

$$C_6H_5\cdot N_2\cdot NH\cdot C_6H_5=C_6H_5\cdot N_2\cdot C_6H_4\cdot NH_2.$$

The manufacture is carried out as follows: 100 kilos. of aniline are mixed with 36 kilos. of concentrated hydrochloric acid, the mixture cooled (from outside) to about 18°, and a solution of 15·5 kilos. of sodium nitrite in 18 kilos. of water and 18 kilos. of saturated sodium chloride solution added at first fairly rapidly, so that the temperature rises to 25°, and then more slowly, the temperature being kept below 28° by outside cooling. This operation takes about 7–8 hours. After 24 hours the change of diazoaminobenzene into aminoazobenzene is complete. The salt solution is now drawn off, the residue stirred with 96 kilos. of hydrochloric acid and 64 kilos. of water, and the aminoazobenzene hydrochloride is filtered off, washed with 2 p.c. hydrochloric acid, centrifuged and dried at 60°. The yield is 41 kilos. of dry aminoazobenzene hydrochloride. The old aniline yellow was the oxalate of the base. The free base crystallises in yellow rhombic prisms. M.p. 127·4°; b.p. above 300°. The hydrochloride crystallises in steel-blue needles. Base slightly

soluble in hot water, readily soluble in alcohol. Yellow solution coloured red by hydrochloric acid.

Literature.—Mène, 1861 (*see* above); Dale and Caro, E. P. 3307 of 1863; Martius und Griess, Zeitsch. f. Chem. 1866, 2, 132; Kekulé *ibid.* 2, 689; Witt and Thomas, Chem. Soc. Trans. 1883, 43, 112; Friswell and Green, *ibid.* 1885, 47, 917; and 1886, 49, 746; Städel and Bauer, Ber. 1886, 19, 1953.

Butter Yellow; **Oil Yellow** (W.); Dimethylaminoazobenzene, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$. Prepared by the action of diazobenzene chloride on dimethylaniline. Substance forms yellow leaflets of m.p. 115°; soluble in dilute hydrochloric acid with a red colour; precipitated by alkali. Soluble in strong sulphuric acid with a yellow colour, becoming red on dilution.

Literature.—Griess, Ber. 1877, 10, 528.

Chrysoïdine (most firms); **Chrysoïdine Y** (H.) (W.); **Chrysoïdine JEE** (C. J.); **Chrysoïdine Crystals**;[1] **Chrysoïdine Small Crystals** (T. M.)

Diaminoazobenzene $C_6H_5{\cdot}N_2{\cdot}C_6H_3(NH_2)_2$. [1] [2:4]

This colouring matter is prepared by mixing a solution of diazobenzene chloride with a solution of *m*-phenylenediamine. In practice a known weight of aniline is dissolved in dilute hydrochloric acid and diazotised, the solution being diluted so as to contain about 2–3 p.c. of diazo- salt. This and a dilute solution of phenylenediamine hydrochloride are run simultaneously into a sodium chloride solution, and the colouring matter is filtered off through a filter press. The press cake is then dissolved in hot dilute hydrochloric acid, the hot solution filtered, and hydrochloric acid added to the filtrate. The chrysoïdine separates in small needles, which are filtered off, centrifuged, and dried at 50°. The free base forms yellow needles; m.p. 117·5°. Slightly soluble in water, readily in alcohol; solutions orange. The commercial product is the hydrochloride $C_{12}H_{12}N_4{\cdot}HCl$, which forms beautiful blackish-green prisms with a metallic lustre. The strong solution of the salt solidifies on rapid cooling to a red jelly. Dissolves in strong sulphuric acid with a brownish-yellow colour.

Literature.—Hofmann, Ber. 1877, 10, 213; Witt, *ibid.* 350 and 654; Griess, *ibid.* 389.

Chrysoïdine R (H.) (W.) (G.) (I.); **Chrysoïdine REE** (P.); **Cerotine Orange** (C. J.); **Gold Orange for Cotton** (T. M.) (D. H.); Benzeneazo-*m*-tolylenediamine $C_6H_5{\cdot}N_2{\cdot}C_6H_2(CH_3)(NH_2)_2$. Prepared from aniline and *m*-tolylenediamine as in the preceding case. The free base melts at 165°–166°. The commercial product is the hydrochloride, which forms yellowish-brown lumps. Dissolves in strong sulphuric acid with a greenish-yellow colour.

Chrysoïdine R (D. H.); Tolueneazo-*m*-tolylenediamine $CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(CH_3)(NH_2)_2$. Prepared as above from *o*-toluidine and *m*-tolylenediamine. The commercial product is the hydrochloride. It is a crystalline violet powder which gives a brown colour in strong sulphuric acid.

Meta Chrome Brown B (A.): Dinitrophenolazo-*m*-tolylenediamine

$OH{\cdot}C_6H_2(NO_2)_2N_2{\cdot}C_6H_2(CH_3)(NH_2)_2$.

Prepared from picramic acid and *m*-tolylenediamine. It is a brown paste giving a dark orange-red solution in hot water. It yields a red solution with strong sulphuric acid.

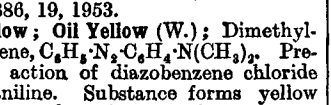
[1] Chrysoïdine Crystals also contain the homologues form *o*- and *p*-toluidine.

Literature.—E. P. 22886 of 1899; D. R. P. 112819.

Chrome Brown P (P.); Dinitrophenolazo-*m*-aminophenol $OH{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}NH_2$. Prepared from picramic acid and *m*-aminophenol. Introduced in 1903.

Literature.—D. P. 169579; F. P. 336559.

Diazine Green (K.); **Janus Green B** (M.):



Prepared from diazotised diethylsafranine and dimethylaniline. The commercial product is a brown or dark-green powder giving an olive-green solution with strong sulphuric acid. **Janus Green G** is a dyestuff of analogous constitution.

Literature.—E. P. 7337 of 1897; F. P. 265438; D. R. P. 95668.

II. Acid Azo- Compounds.

A. Sulphonic Acids of Aminoazo- Compounds.

Acid Yellow (A.); **Fast Yellow** (B.) (By.); **Fast Yellow G**; **New Yellow L** (K.); **Yellow SS** (P.); **Fast Yellow extra** (By.). This colouring matter is a mixture of the sodium salts of mono- and di- sulphonic acids of aminoazobenzene

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$ and $HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(HSO_3){\cdot}NH_2$.

Prepared by the action of fuming sulphuric acid on aniline yellow (3–5 parts acid to one of aminoazobenzene). Solution not precipitated by alkali; colour dissolves in strong sulphuric acid with a brownish-yellow colour becoming redder on dilution. Solution gives a precipitate with barium chloride, but not with calcium chloride. The corresponding colouring matter from aminoazotoluene is somewhat more orange in shade, and is known as **Fast Yellow** (B.); **Yellow W** (By.); **Fast Yellow R** (K.).

Literature.—Grässler, E. P. 43 of 1879; A. P. 253598; D. R. P. 4186, 7094; Chem. Ind. 1879, 2, 48, 346; Griess, Ber. 1882, 15, 2187; Eger. Ber. 1889, 22, 847.

Methyl Orange; **Helianthin**; **Orange III.**; **Gold Orange**; *p*-Sulphobenzeneazodimethylaniline $HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$. [4] [1] [4] Prepared by the action of diazotised sulphanilic acid[1] on dimethylaniline. Solution of colouring matter orange, and not precipitated by alkali; dilute acids produce a crystalline precipitate, the crystals having a violet reflexion (the free sulphonic acid). The substance dissolves in strong sulphuric acid with a yellow colour becoming red on dilution.

Literature.—Griess, Ber. 1877, 10, 528.

Tropæoline OO (C.); **Orange IV.** (P.); **Diphenylamine Orange**; **Acid Yellow D** (A.); **Orange N** (B.); **New Yellow** (By.); **Orange M** (I.); *p*-Sulphobenzeneazodiphenylamine

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}\underbrace{NH{\cdot}C_6H_5}_{[4]}$. [4] [1]

[1] For detailed information on the manufacture of sulphanilic acid and its homologues *see* Mühlhäuser, Dingl. poly. J. 1887, 264, 181 and 238; Paul, Zeitsch. angew. Chem. 1896, 9, 686.

Produced by the action of diazotised sulphanilic acid on diphenylamine dissolved in alcohol or crude carbolic acid. The product is thrown on an open filter, the paste dissolved in concentrated aqueous potassium carbonate and precipitated by adding sodium hydroxide. The colouring matter is not very readily soluble in water; the solution is yellow, and when strong deposits crystals on cooling. Substance dissolves in strong sulphuric acid with a violet colour, becoming redder and giving a greyish precipitate of the free sulphonic acid on dilution. The aqueous solution of the substance is coloured red by dilute acids.

When nitrated this colour furnishes a mono-nitro- derivative together with a mixture of mono-, di-, and tri- nitrodiphenylamine; moderate nitration yields a yellow colouring matter which is found in commerce under the names of **Citronine** (O.); **Curcumeïne** (A.); **Azoflavine 3 R** ex. conc. (T. M.); **Citronine NE** (P.). More energetic nitration of Orange IV. furnishes **Azo Acid Yellow** (A.); **Azo Yellow** (M.); **Azo Yellow 3 G, ex. conc.** (T. M.); **Citronine 2 AEJ** (P.); **Azoflavine** (B.); **Indian Yellow** (By.). Both dyestuffs are ochre-yellow powders and give with strong sulphuric acid reddish-violet and magenta-red solutions respectively.

Metanil Yellow (O.), (B.), (A.), (C. J.); **Orange MN** (I.); **Tropæoline G** (C.); **Yellow M** (P.); **Metanil Yellow GR extra** (T. M.).; *m*-Sulphobenzeneazodiphenylamine

$$HSO_3\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH\cdot C_6H_5.$$
[3] [1] [4]

Prepared in the same manner as the preceding from *m*-diazobenzenesulphonic acid[1] and diphenylamine. Aqueous solution orange, giving no precipitate with alkalis, becoming red and precipitating with dilute acids. Dissolves in strong sulphuric acid with a dull violet colour, becoming magenta-red on dilution.

Metanil Yellow S; **Acid Yellow 2 G**, is produced by sulphonating the preceding colouring matter.

Literature.—E. P. 1226 of 1879; 4966 of 1880; Paul, Zeitsch. angew. Chem. 1896, 9, 686.

Fast Yellow N (P.); **Jaune Solide N**; **Curcumeïne**; Sulphotoluneneazodiphenylamine

$$HSO_3\cdot C_7H_6\cdot N_2\cdot C_6H_4\cdot NH\cdot C_6H_5$$
[1] [4]

This colouring matter is homologous with the two preceding, which it resembles in its general properties.

Literature.—Roussin and Poirrier, E. P. 4491 of 1878.

Archil Substitute V; *p*-Nitrobenzeneazo-*a*-naphthylamine-*p*-sulphonic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(NH_2)\cdot HSO_3.$$

Prepared by the action of diazotised *p*-nitroaniline on naphthionic acid[2] in weakly acid solution. Solution precipitated by acids and alkalis. Strong sulphuric acid gives a magenta-red solution, becoming brownish and precipitating on dilution.

[1] *m*-Aminobenzenesulphonic acid is prepared by sulphonating nitrobenzene and reducing the *m*-nitrobenzenesulphonic acid thus formed.

[2] Naphthionic acid is manufactured on a large scale by heating *a*-naphthylamine with 3–4 parts of strong sulphuric acid or by heating dry naphthylamine sulphate to 180°–200°.

Literature.—Roussin and Poirrier, E. P. 4490 of 1878; D. R. P. 6715; F. P. 127221; Chem. Ind. 1879, 2, 292.

Archil Substitute 3 VN (P.); **Archil Substitute V** (A.);. *p*-Nitrobenzeneazo-*a*-naphthylaminesulphonic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(NH_2)\cdot SO_3H.$$

Prepared by the action of diazotised *p*-nitroaniline on *a*-naphthylamine-5-sulphonic acid. Forms a brown powder giving a red solution in water or strong sulphuric acid.

Literature.—E. P. 12692 of 1887; D. R. P. 45787; F. P. 185908.

Palatine Chrome Brown W (B.); *p*-Sulpho-*o*-hydroxybenzeneazo-*m*-phenylenediamine

$$SO_3H\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_3(NH_2)_2.$$

Prepared from diazotised *o*-aminophenol-*p*-sulphonic acid and *m*-phenylenediamine. A black-brown powder dissolving in hot water with an orange-brown colour, and in strong sulphuric acid to give a dark orange-brown solution.

Literature.—A. P. 628814; F. P. 284741.

Anthracyl Chrome Green (D.); Dinitrophenolazo-*a*-naphthylamine-4-sulphonic acid

$$OH\cdot C_6H_2(NO_2)_2\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2.$$

Prepared by the action of diazotised picramic acid on naphthionic acid. Solution in water is reddish-brown, and in strong sulphuric acid bluish fiery red.

Literature.—D. P. 142153.

Alkali Brown (D.); **Benzo Brown 5 R** (By.); **Alkali Brown R** (L. P.); **Cotton Brown R** (B.); **Terra Cotta** (G.); Primulineazo-*m*-phenylenediamine P[1] $\cdot N_2\cdot C_6H_3(NH_2)_2$. Prepared from diazotised primuline or dehydrothio-*p*-toluidinesulphonic acid on *m*-phenylenediamine. Solution brownish-red, precipitated by acids or alkalis. Gives a bluish-violet solution with strong sulphuric acid.

Apollo Red (G.); **Archil Substitute extra** (C.); *p*-Nitrobenzeneazo-a-naphthylaminedisulphonic acid, $NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(NH_2)(SO_3H)_2$. Prepared from diazotised *p*-nitroaniline and *a*-naphthylamine-4 : 6- or 4 : 7-disulphonic acid. Gives a brownish-red solution in water and a magenta-red in strong sulphuric acid.

Literature.—E. P. 9468 of 1887; A. P. 376392; F. P. 184638.

Brilliant Archil C (C.); **Brilliant Wool Scarlet** (K); Azimide of *p*-nitrobenzeneazo-1 : 8-naphthylenediaminedisulphonic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\begin{matrix}N\\ \diagdown\\ \diagup\\ N\end{matrix}\!\!>\!N.$$

Prepared by the action of nitrous acid on the product from diazotised *p*-nitroaniline and 1 : 8-naphthylenediamine-3 : 6-disulphonic acid. A brownish-red powder dissolving in water with a red, and in strong sulphonic acid with a blue, solution.

Literature.—E. P. 24714 of 1893; D. R. P. 77425; F. P. 234837.

Wool Violet S (B.); Dinitrobenzeneazo diethylmetanilic acid

$$(NO_2)_2C_6H_2\cdot N_2\cdot C_6H_3(SO_3H)\cdot N(C_2H_5)_2.$$

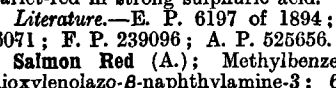
Prepared from diazotised 2 : 4-dinitroaniline and diethylmetanilic acid. A black powder

[1] P = the residue of primuline.

giving a reddish-violet solution in water and a scarlet-red in strong sulphuric acid.

Literature.—E. P. 6197 of 1894; D. R. P. 86071; F. P. 239096; A. P. 525656.

Salmon Red (A.); Methylbenzenylaminothioxylenolazo-β-naphthylamine-3: 6-disulphonic acid



Prepared from diazotised dehydrothio-*m*-xylidine and β-naphthylamine-3: 6-disulphonic acid R. Aqueous solution is orange red. Gives violet solution in strong sulphuric acid.

Literature.—Paul, Zeitsch. angew. Chem. 1896, 9, 680.

Brilliant Yellow S (B.) (T. M.); **Yellow WR** (I.); **Curcumine** (G.); *p*-Sulphobenzeneazodiphenylaminesulphonic acid. Prepared by sulphonating orange IV. Solution in water is yellow and in strong sulphuric acid bluish-red.

Literature.—D. R. P. 21903.

Lanacyl Violet B (C.); Disulphohydroxynaphthaleneazoethyl-α-naphthylamine

$$(HSO_3)_2C_{10}H_4(OH)\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_2H_5.$$

Prepared from diazotised 1: 8-aminonaphthol-3: 6-disulphonic acid and ethyl-α-naphthylamine. Solution in water is reddish-violet, and in strong sulphuric acid is greenish-blue.

Literature.—E. P. 12556 of 1896; D. R. P. 94288; F. P. 257136.

B. Carboxylic Acids of Aminoazo- Compounds.

Yellow fast-to-soap (P.); **Orange MG** (P.); *m*-Carboxybenzeneazodiphenylamine

$$CO_2H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH\cdot C_6H_5.$$

Prepared by the action of *m*-diazobenzoic acid on diphenylamine. Used in wool-dyeing and especially calico-printing; the shades are very fast to soap. A brown paste, difficultly soluble in water. Solution becomes reddish-violet with acids. Dissolves with a violet colour in strong sulphuric acid, becoming red on dilution.

Literature.—E. P. 4621 of 1883; D. R. P. 29991; F. P. 157755; A. P. 297852.

C. Hydroxyazo- Compounds.

Sudan Brown (A.); **Pigment Brown** (B.); α-Naphthaleneazo-α-naphthol

$$C_{10}H_7\cdot N_2\cdot C_{10}H_6\cdot OH.$$

Prepared by the action of diazotised α-naphthylamine on α-naphthol in alkaline solution.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799; Frankland, Trans. Chem. Soc. 1880, 37, 752.

Sudan G (A.) (F.) (Ib.) (W.); **Carminaph J** (D. H.); **Cerasine Orange G** (C.); **Cerotine Yellow R** (C. J.); **Chrysoïn insoluble** (P.); Benzeneazoresorcinol $C_6H_5\cdot N_2\cdot C_6H_3(OH)_2$. Prepared by the action of diazobenzene chloride on resorcinol in alkaline solution. Solution of colouring matter yellow, giving a brown precipitate with acids. Dissolves in strong sulphuric acid with a yellowish-brown colour.

Literature.—Baeyer and Jäger, Ber. 1875, 8, 151; Typke, *ibid.* 1877, 10, 1576; Wallach, *ibid.* 1881, 14, 24; Wallach and Fischer, *ibid.* 1882, 15, 2814; Meyer and Kreis, *ibid.* 1883, 16, 1329; Liebermann and Kostanecki, *ibid.* 1884, 17, 880; Heumann and Oeconomides, *ibid.* 1887, 20, 904; Will and Pukall, *ibid.* 1120; Pukall, *ibid.* 1147; Fischer and Wimmer, *ibid.* 1578; Will, *ibid.* 1888, 21, 604; Kostanecki, *ibid.* 3119.

Sudan I (A.) (F.) (Ib.) (K.) (W.); **Carminaph** (D. H.); **Cerotine Orange G** (C. J.); Benzeneazo-β-naphthol $C_6H_5\cdot N_2\cdot C_{10}H_6\cdot OH$. Prepared from diazobenzene chloride and β-naphthol. A brick-red powder insoluble in water. Used for colouring oils, &c.

Literature.—Liebermann, Ber. 1883, 16, 2860; Denare, Gazz. chim. ital. 1885, 15, 406; Zincke and Bindewald, Ber. 1884, 17, 3031; Zincke and Rathgen, *ibid.* 1886, 19, 2484; Fischer and Wimmer, *ibid.* 1887, 20, 1579; Weinberg, *ibid.* 3172; Jacobson, *ibid.* 1888, 21, 415; Meldola and East, Trans. Chem. Soc. 1888, 53, 460; Meldola and Morgan, *ibid.* 1889, 55, 603; Goldschmidt and Rosell, Ber. 1890, 23, 496; Goldschmidt and Brubacher, *ibid.* 1891, 24, 2306; McPherson, Ber. 1895, 28, 2418; Farmer and Hantzsch, *ibid.* 1899, 32, 3100; Möhlau and Strohbach, *ibid.* 1900, 33, 805; Goldschmidt and Keppeler, *ibid.* 894; Möhlau and Kegel, *ibid.* 2873; Betti, Gazz. chim. ital. 1900, 30, ii. 164.

Sudan II (A.) (K.); **Red B** (B.) (Fi.); **Cerotine Scarlet G** (C. J.); Xyleneazo-β-naphthol

$$C_6H_3(CH_3)_2\cdot N_2\cdot C_{10}H_6\cdot OH.$$

Prepared from diazotised xylidine and β-naphthol.

Carminaph Garnet (D. H.); **Cerotine Scarlet 2 R** (C. J.); α-Naphthaleneazo-β-naphthol

$$C_{10}H_7\cdot N_2\cdot C_{10}H_6\cdot OH.$$

Prepared from diazotised α-naphthylamine and β-naphthol. An insoluble paste used in printing. (*See* also **Naphthylamine Bordeaux**, p. 363.)

Azophosphine GO (M.) Chloride of *m*-trimethylaminobenzeneazoresorcinol

$$ClN(CH_3)_3\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)_2.$$

Prepared from diazotised *m*-aminophenyltrimethylammonium chloride and resorcinol. Solution in water is yellowish-red, and in strong sulphuric acid brownish-red.

Literature.—E. P. 14494 of 1895; D. R. P. 87257; F. P. 249227.

New Phosphine G (C.); ω-Dimethylaminotolueneazoresorcinol,

$$N(CH_3)_2\cdot CH_2\cdot C_6H_4\cdot N_2.C_6H_3(OH)_2.$$

Prepared from diazotised *p*-aminobenzyldimethylamine and resorcinol. Gives a yellowish-brown solution in water and strong sulphuric acid.

Literature.—E. P. 22572 of 1892; D. R. P. 70678; F. P. 225968; A. P. 515100.

Tannin Orange R (C.); ω-Dimethylaminotolueneazo-β-naphthol

$$N(CH_3)_2\cdot CH_2\cdot C_6H_4\cdot N_2.C_{10}H_6\cdot OH.$$

Prepared from diazotised *p*-aminobenzyldimethylamine and β-naphthol. A brown powder or a 50 p.c. paste. Sparingly soluble in water, with a browncolour. Gives a yellowish-brown solution in strong sulphuric acid.

Literature.—*As for the preceding colour.*

Azochromine (G.); Tetrahydroxyazobenzene $OH\cdot C_6H_4\cdot N_2\cdot C_6H_2(OH)_2$. Prepared from diazotised *p*-aminophenol and pyrogallol. Commercial product is a 30 p.c. paste, giving a dark-yellow solution in boiling water. With strong sulphuric acid it gives a brown solution.

Literature.—E. P. 11902 of 1893; D. R. P. 81109; F. P. 230937; A. P. 548460.

Diazine Black (K.); **Janus Grey B** (M.); Safranineazophenol. Prepared from one of the varieties of safranine and phenol. Its solution in water is blackish-green blue, and in strong sulphuric acid green.

Literature.—Mon. Sci. 1886, (iii.) 16, 984.

Indoine Blue R (B.) (G.); **Janus Blue** (M.); **Naphthindone** (C.); **Bengaline** (K.); **Vac Blue** (H.); **Fast Cotton Blue R** (O.); **Indole Blue R** (A.); **Diazine Blue** (K.); **Madras Blue P** (P.); Safranineazo-β-naphthol. Prepared from various safranines and β-naphthol. It gives a violet solution in water, and a greenish-brown in strong sulphuric acid.

Literature.—E. P. 4543 of 1891, 18769 of 1893, 3488 of 1895, 23985 of 1898; D. R. P. 61692, 85690, 85932, 91721, 92015, 105433, 108497; F. P. 212276, 245239, 250239, 283013, 285360; A. P. 524251, 524254; Walter, Aus der Praxis der Anilinfarbenfabrikation, 1903, 306 (where the preparation is described in detail).

D. Sulphonic Acids of Hydroxyazo- Compounds.

1. Monosulphonic Acids.

Tropæoline O (C.); **Resorcin Yellow** (A.); **Chrysoïn** (B.); **Chryseoline**; **Gold Yellow** (By.); **Yellow T** (I.); **Acme Yellow** (L.); *p*-Sulphobenzeneazoresorcinol $HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH)_2$. Produced by the action of diazotised sulphanilic acid on resorcinol in alkaline solution. Solution of colouring matter orange; substance dissolves in strong sulphuric acid with a yellow colour.

Literature.—Griess, Ber. 1878, 11, 2195; Witt, Trans. Chem. Soc. 1879, 35, 183.

Orange II (most firms); **Tropæoline OOO, No. 2**; **Betanaphthol Orange**; **Mandarin G Extra** (A.); **Gold Orange** (By.); **Orange Extra** (C.); **Orange A** (L.); **Gold Orange extra conc.** (T.M.); *p*-Sulphobenzeneazo-β-naphthol

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared from diazotised sulphanilic acid and β-naphthol. Solution orange, becoming red on addition of sodium hydroxide. Solution in strong sulphuric acid red, becoming orange on dilution.

Literature.—Hofmann, Ber. 1877, 10, 1378; Griess, *ibid.* 1878, 11, 2198; Witt, *ibid.* 1879, 12, 259; Miller, *ibid.* 1880, 13, 268; Witt, Chem. Zeit. 1880, 4, 437; Mühlhäuser, Dingl. Poly. J. 1887, 264, 181, 238; Paul, Zeitsch. angew. Chem. 1896, 9, 686 (the last two papers give details of the manufacture).

Orange R (I.); **Orange T** (K.); **Kermesin Orange** (L.); **Mandarin GR** (A.); Sulpho-*o*-tolueneazo-β-naphthol

$$HSO_3{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta).$$

Homologous with the preceding, the diazotised sulphonic acid of *o*-toluidine being used instead of sulphanilic acid.

Orange 2 R (I.); **Orange R** (B.); Sulphoxyleneazo-β-naphthol $HSO_3{\cdot}C_8H_8{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta)$. Prepared in the same manner as the preceding from the sulphonic acid of commercial xylidine and β-naphthol. Aqueous solution gives a reddish-brown precipitate with dilute acids. Dissolves with a red colour in strong sulphuric acid, giving a brown precipitate on dilution.

Literature.—The manufacture of the two last colouring matters is described in the paper by Mühlhäuser already referred to.

Azofuchsine B (By); Tolueneazo-1 : 8-dihydroxynaphthalenesulphonic acid

$$CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(OH)_2{\cdot}SO_3H.$$

Prepared by the action of diazotised commercial toluidine on 1 : 8-dihydroxynaphthalene-4-sulphonic acid. Solution in water is bluish-red, and in strong sulphuric acid violet.

Literature.—E. P. 18517 of 1889; D. R. P. 54110; F. P. 203744; A. P. 466841, 468142.

Ponceau 4 GB (A.) (Lev.); **Croceïne Orange** (By.) (C.); **Brilliant Orange G** (M.) (C.J.); **Orange GRX** (B.); Benzeneazo-β-naphtholsulphonic acid

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\beta).$$

Prepared by the action of diazobenzene chloride on β-naphthol-6-sulphonic acid (Schäffer's acid) in alkaline solution. Solutions in water or strong sulphuric acid are orange-yellow.

Literature.—Griess, Ber. 1878, 11, 2197.

Orange GT (By.); **Orange RN** (C.); **Orange O** (M.); Tolueneazo-β-naphthol-sulphonic acid $C_7H_7{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\beta)$. Prepared by diazotising commercial toluidine and combining with Schäffer's β-naphtholmonosulphonic acid in alkaline solution. Orange aqueous solution gives an oily precipitate with acids. Dissolves in strong sulphuric acid with a magenta-red colour, giving an oily deposit on dilution.

Scarlet GR (A.); **Scarlet R** (By.); **Brilliant Orange R** (M.) (C. J.); **Orange L** (Lev.) (P.). Homologous with the last; prepared from diazotised xylidine and Schäffer's acid. Dissolves in strong sulphuric acid with a red colour, becoming brown and precipitating on dilution.

Literature.—Levinstein, Ber. 1880, 13, 586.

Azococcine 2 R (A.); **Double Scarlet R** (Lev.); Xyleneazo-α-naphtholsulphonic acid

$$(CH_3)_2C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\alpha).$$

Prepared by the action of diazoxylene chloride (commercial xylidine diazotised) on α-naphthol-4-sulphonic acid in alkaline solution. Aqueous solution not precipitated by alkalis; when hot and concentrated deposits bronzy crystals on cooling. Dissolves in strong sulphuric acid with a reddish-violet colour, becoming brown and precipitating free acid on dilution.

Literature.—E. P. 2237 of 1883; D. R. P. 26012.

Azo Grenadine L (By.); Acetylaminobenzeneazo-α-naphthol-4-sulphonic acid

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared from diazotised *p*-aminoacetanilide and α-naphthol-4-sulphonic acid. Magenta-red aqueous solution becomes orange-red with sodium hydroxide. Solution in strong sulphuric acid is red.

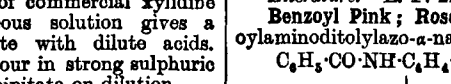
Azoeosine (By.) (Lev.); **Azoeosine G** (K.); Anisoleazo-α-naphthol-4-sulphonic acid

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared from diazotised *o*-anisidine and α-naphthol-4-sulphonic acid. Gives a red solution in water and a carmine-red in strong sulphuric acid.

Literature.—E. P. 2237 of 1883.

Benzoyl Pink; **Rose de Benzoyl** (P.); Benzoylaminoditolylazo-α-naphthol-4-sulphonic acid



Prepared from diazotised monobenzoyl-*o*-toluidine and α-naphthol-4-sulphonic acid. A brick-

red paste, giving a cherry-red solution in water, and a bluish-red solution in strong sulphuric acid.

Literature.—D. R. P. 60332.

Fast Red BT (By.) (Lev.) (D.H.); α-Naphthaleneazo-β-naphthol-6-sulphonic acid

$$C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared from diazotised α-naphthylamine and β-naphthol-6-sulphonic acid (Schäffer). Gives a red solution in water and a violet in strong sulphuric acid.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799.

Fast Brown N (By.); **Acid Brown O** (M.); **Naphthylamine Brown**; *p*-Sulphonaphthaleneazo-α-naphthol $HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared by the action of diazotised α-naphthylamine-4-sulphonic acid (naphthionic acid) on α-naphthol in alkaline solution. Colouring matter gives a reddish-brown solution, not changed by acids or alkalis. Dissolves in strong sulphuric acid with a reddish-violet colour.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799.

Fast Brown 3 B (A.); Sulphonaphthalene-2-azo-α-naphthol $HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared by the action of diazotised β-naphthylamine-6-sulphonic acid on α-naphthol in alkaline solution.

Aqueous solution brownish-red, becoming violet with dilute acids and red with alkalis. Solution in strong sulphuric acid blue, giving reddish-violet precipitate on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547; F. P. 150503; A. P. 332829.

Chrome Fast Cyanine G (I.), introduced into commerce in 1907, is prepared by the action of diazotised 1-amino-2-naphtholsulphonic acid on α-naphthol.

Eriochrome Blue Black B (G.); Sulphonaphtholazo-α-naphthol

$$HSO_3{\cdot}C_{10}H_5(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared by the action of diazotised 1-amino-β-naphthol-4-sulphonic acid on α-naphthol.[1] The blackish-violet aqueous solution on addition of hydrochloric acid becomes first reddish-brown, and then gives a brownish-black precipitate. With sodium hydroxide the solution becomes first blue and, on adding excess, finally red. The solution in strong sulphuric acid is blue, giving a violet-black precipitate on dilution.

Literature.—E. P. 15025 of 1904; D. R. P. 181326; F. P. 350055; Ital. P. 73530; Aust. P. 30630.

Eriochrome Black T (G.); Nitrosulphonaphtholazo-α-naphthol

$$NO_2{\cdot}C_{10}H_4(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared by the action of diazotised 8-nitro-amino-β-naphthol-4-sulphonic acid on α-naphthol. The reddish-brown aqueous solution gives a violet-brown precipitate with hydrochloric acid, and, with sodium hydroxide, becomes first deep-blue and then red. The solution in strong sulphuric acid is blackish-blue, giving a brown precipitate on dilution.

Literature.—E. P. 15982 of 1904; D. R. P. 169683; F. P. 350071; Ital. P. 73531; Aust. P. 27191.

Brilliant Double Scarlet G (A.) (Lev.) (K.); **Scarlet for silk** (M.); **Ponceau for silk** (P.). Prepared from β-naphthylamine-6-sulphonic acid and β-naphthol. Aqueous solution gives brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour, giving a brown precipitate on dilution.

Literature as under **Fast Red B.**

Fast Red; **Fast Red A** (B.) (C. J.) (Lev.); **Roccelline** (D. H.); **Rauracienne**; **Rubidine**; Sulphonaphthaleneazo-β-naphthol

$$HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared by the action of diazotised naphthionic acid on β-naphthol in alkaline solution. Substance dissolves in hot water with a reddish-brown colour; concentrated solution when rapidly cooled solidifying to a brown gelatinous mass. Soluble in strong sulphuric acid with a violet colour, becoming brown and giving a precipitate of the free acid on dilution. The corresponding colouring matter from α-naphthylamine-5-sulphonic acid is called **Brilliant Fast Red G** (B.).

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799; Griess, Ber. 1878, 11, 2199; 1879, 12, 1364.

Acid Ponceau (D. H.); **Fast Acid Scarlet**; **Ponceau S for silk** (I.); **Ponceau G for Silk** (K.); Sulpho-β-naphthaleneazo-β-naphthol

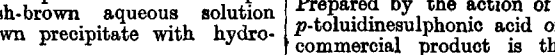
$$HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared by sulphonating β-naphthylamine, diazotising the mixed isomeric sulphonic acids, and combining with β-naphthol in alkaline solution. Aqueous solution gives a brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour, becoming brown and precipitating on dilution.

Lithol Red B (B.); Sulphonaphthaleneazo-β-naphthol $HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared by the action of diazotised β-naphthylamine-1-sulphonic acid on β-naphthol. The commercial product is a paste which is only very sparingly soluble even in hot water. It is used exclusively in the manufacture of lakes.

Literature.—E. P. 25511 of 1899; D. R. P. 112833; F. P. 297330; A. P. 650757.

Clayton Cloth Red (Cl. Co.); **Stanley Red** (Cl. Co.); Sulphobenzenylaminothiocresolazo-β-naphthol



Prepared by the action of diazotised dehydro-*p*-toluidinesulphonic acid on β-naphthol. The commercial product is the ammonium salt. Forms a reddish-brown solution in water, and a violet-red with strong sulphuric acid.

Literature.—E. P. 18901 of 1889; D. R. P. 51331.

Acid Alizarine Black R (M.); Nitrosulphophenolazo-β-naphthol

$$OH{\cdot}C_6H_2(NO_2)(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared from diazotised 6-nitro-2-aminophenol-4-sulphonic acid and β-naphthol. Aqueous

[1] In the constitutional formula of this colouring matter, kindly communicated along with other information to the writer by the manufacturers, the azo- group is shown attached to the 2- position of the α-naphthol, although the 4- position is unoccupied. The combination is probably effected in presence of very concentrated alkali hydroxide. Other examples of this ortho- combination are known, both in the benzene and naphthalene series. (Compare Michel and Grandmougin, Ber. 1893, 26, 2353; Bamberger, *ibid.* 1900, 33, 3188; Bamberger and Meimberg, *ibid.* 1895, 28, 1889; Bamberger, *ibid.* 848; D. P. 14443.)

solution is brownish-violet, and solution in strong sulphuric acid is reddish-violet.

Literature.—E. P. 2772 of 1900; D. R. P. 143892; A. P. 667935.

Anthracene Chrome Black (C.); Sulphonaphtholazo-β-naphthol

$$HSO_3 \cdot C_{10}H_5(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared by the action of diazotised 3-amino-β-naphthol-7-sulphonic acid (R.) on β-naphthol. Aqueous solution is red; hydrochloric acid gives a reddish-violet precipitate, and sodium hydroxide turns it bluish-violet. Solution in strong sulphuric acid is bluish-green, giving a reddish-violet precipitate on dilution.

Literature.—E. P. 28107 of 1897; D. R. P. 109932; F. P. 272620, 272621.

Palatine Chrome Blue (B.); **Eriochrome Blue Black R** (G.). Isomeric with the preceding. Prepared from diazotised 1-amino-β-naphthol-4-sulphonic acid and β-naphthol. Blue aqueous solution gives yellowish-brown precipitate with hydrochloric acid, and turns first blue and then red with sodium hydroxide. Solution in strong sulphuric acid is dark blue, giving a blackish-brown precipitate on dilution.

Literature.—E. P. 15025 of 1904; F. P. 350055; Ital. P. 73530; Aust. P. 30630.

Salicin Black U (K.) is the zinc sodium salt of the above, and is prepared by diazotising 1-amino-β-naphthol-4-sulphonic acid with zinc nitrite and combining the diazo-compound with β-naphthol in concentrated alkaline solution.

Literature.—E. P. 23034 of 1905; D. R. P. 175593, 195228; F. P. 353786; A. P. 807422.

Eriochrome Black A (G.); Nitrosulphonaphtholazo-β-naphthol

$$NO_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared from diazotised 8-nitro-1-amino-β-naphthol-4-sulphonic acid and β-naphthol. Dark-blue aqueous solution gives a reddish-brown precipitate with hydrochloric acid, and becomes cherry-red with sodium hydroxide. Solution in strong sulphuric acid is dark-violet blue, giving a brown precipitate on dilution.

Literature.—E. P. 15982 of 1904; D. R. P. 169683; F. P. 350071; A. P. 790363; Ital. P. 73531; Aust. P. 27191.

Diamond Black PV (By.); Sulphophenolazo-1 : 5-dihydroxynaphthalene

$$OH \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_{10}H_5(OH)_2.$$

Prepared from diazotised o-aminophenolsulphonic acid and 1 : 5-dihydroxynaphthalene. Bluish-red aqueous solution gives a dark red precipitate with hydrochloric acid. Solution in strong sulphuric acid is blackish-green, giving a reddish precipitate on dilution.

Literature.—E. P. 18139 of 1902.

Roxamine (D. H.); Sulphonaphthaleneazo-2 : 7-dihydroxynaphthalene

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(OH)_2.$$

Prepared by the action of diazotised naphthionic acid on 2 : 7-dihydroxynaphthalene. Aqueous solution is scarlet. Dissolves in strong sulphuric acid with a violet colour.

Azo Acid Blue 4 R (By.). Is probably prepared by the action of diazotised p-nitroaniline on 1 : 8-dihydroxynaphthalene-4-sulphonic acid and subsequently reducing the nitro- group. It gives a blue-violet solution in water and a reddish-violet in strong sulphuric acid.

Literature.—Chem. Ind. 1896, 19, 549.

Milling Yellow (Lev.) (D.); **Chrome Yellow D** (By.); **Anthracene Yellow BN** (C.); **Mordant Yellow O** (B.) (M.); **Chrome Fast Yellow** (A.); **Salicin Yellow D** (K.); Sulphonaphthaleneazosalicylic acid

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared by the action of diazotised β-naphthylamine-5-(or 6)-sulphonic acid on salicylic acid. Solution in water is yellow, and in strong sulphuric acid yellowish-red.

Oriol Yellow (G.); **Cotton Yellow R** (B.); **Alkali Yellow** (D.); Primulineazosalicylic acid $P^{1} \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$. Prepared by the action of diazotised primuline on salicylic acid. Gives an orange-yellow solution in water, and a scarlet-red with strong sulphuric acid.

Literature.—D. R. P. 48465; F. P. 192628; A. P. 398990.

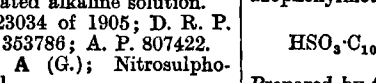
Eriochrome Phosphine R (G.); Nitrosulphobenzeneazosalicylic acid

$$NO_2 \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared by the action of diazotised p-nitroaniline-o-sulphonic acid on salicylic acid. Yellowish-orange aqueous solution becomes pale orange with hydrochloric acid, and blue-red with sodium hydroxide. Solution in strong sulphuric acid is yellowish orange giving a pale-yellow precipitate on dilution.

Literature.—D. R. P. appl. A 17781 of 1909.

Eriochrome Red B (G.); Sulphonaphtholazophenylmethylpyrazolone



Prepared by the action of diazotised 1-amino-β-naphthol-4-sulphonic acid on phenylmethylpyrazolone. Yellowish-red aqueous solution gives a bright scarlet-red precipitate with hydrochloric acid, and becomes orange-yellow with sodium hydroxide. Solution in strong sulphuric acid is magenta-red, giving a scarlet-red precipitate on dilution.

Literature.—E. P. 17274 of 1904; D. R. P. 165743; F. P. 350161; A. P. 808919.

Dianil Yellow R (M.). Prepared by the action of diazotised primuline (sulphonic acid) on 1-phenyl-3-methylpyrazolone. The orange-yellow aqueous solution gives an orange-yellow precipitate with hydrochloric acid and a reddish-yellow one with sodium hydroxide. Solution in strong sulphuric acid is dark orange, giving an orange-yellow precipitate on dilution.

Literature.—E. P. 10127 of 1897; D. R. P. 117575.

Dianil Yellow 3 G (M.). Prepared from diazotised dehydrothio-p-toluidinesulphonic acid and ethyl acetoacetate. Greenish-yellow aqueous solution gives a yellow precipitate with hydrochloric acid, and becomes orange with sodium hydroxide. Solution in strong sulphuric acid is brownish-yellow, giving a yellow precipitate on dilution.

Literature.—E. P. 17328 of 1897; D. R. P. 98761; F. P. 256647, 269001; A. P. 66256.

2. Disulphonic Acids.

Phenoflavine (O.); m-Sulphobenzeneazoaminophenolsulphonic acid.

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(SO_3H)(NH_2) \cdot OH.$$

[1] P = residue of primuline.

Prepared by the action of diazotised metanilic acid on 3-aminophenol-5-sulphonic acid (III.). Gives a yellow solution in water or strong sulphuric acid.

Literature.—D. R. P. 71229.

Chrome Brown RR (G.); Disulphophenolazopyrogallol

$$OH\cdot C_6H_3(SO_3H)_2\cdot N_2\cdot C_6H_2(OH)_3.$$

Prepared by the action of diazotised *p*-aminophenol-2 : 6-disulphonic acid on pyrogallol. Solution in water is yellow, and in strong sulphuric acid brown.

Literature.—E. P. 11902 of 1893; D. R. P. 81109; F. P. 230937; A. P. 548460.

Orange G (A.) (M.) (B.) (P.) (C. J.); **Orange GG** (C.); Benzeneazo-β-naphtholdisulphonic acid $C_6H_5\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH(\beta)$. Produced by the action of diazobenzene chloride on β-naphthol-6 : 8-disulphonic acid (G-salt) in alkaline solution. Solution not precipitated by alkali; dissolves in strong sulphuric acid with an orange colour, undergoing no change on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811.

Crystal Scarlet 6 R (C.) (M.); **Crystal Ponceau** (A.)(K.)(B.); α-Naphthaleneazo-β-naphthol-6 : 8-disulphonic acid (G-acid). Produced by the action of diazotised α-naphthylamine upon β-naphthol-6 : 8-disulphonic acid in alkaline solution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; A. P. 332528.

Ponceau 2 G (A.) (B.) (M.) (C.); **Orange R** (H.). Isomeric with Orange G. Prepared by the action of diazobenzene chloride upon β-naphthol-3 : 6-disulphonic acid (R-salt). Properties similar to those of the preceding compound; colour slightly redder in shade.

Literature as for Orange G.

Azocoralline (D.); *p*-Acetylaminobenzeneazo-β-naphthol-3 : 6-disulphonic acid

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on β-naphthol-3 : 6-disulphonic acid (R-salt). Solution in water is orange-red, and in strong sulphuric acid yellowish-red.

Literature.—Nietzki, Ber. 1884, 17, 344.

Ponceau R, 2 R, G and **GR** [1] (A.) (B.) (M.) (Lev.) (H.) (C.) (C. J.); **Brilliant Ponceau R** (T. M.); **Xylidine Scarlet**; **Xylidine Red**; Xyleneazo-β-naphthol-3 : 6-disulphonic acid

$$C_6H_9\cdot N_2\cdot C_{10}H_4(HSO_3)_2\cdot OH(\beta).$$

Produced by the action of diazotised xylidine (chiefly meta-) on β-naphthol-3 : 6-disulphonic acid (R-salt). Properties similar to those of Orange G. Colour a distinct scarlet; aqueous solution not precipitated by alkali; an amorphous precipitate by calcium or barium chloride. Soluble with a red colour in strong sulphuric acid, becoming brown and precipitating on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811; A. P. 210233.

Ponceau 3 R (A.) (B.) (M.) (C. J.) (K.); **Ponceau 4 R** [2] (A.); **Cumidine Red** (M.); Cumeneazo-β-naphthol-3 : 6-disulphonic acid

$$C_9H_{11}\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH(\beta).$$

[1] **G** and **GR** are made from crude xylidine and crude R-salt, **R** from crude xylidine and **2 R** from *m*-xylidine and pure R-salt.

[2] **3 R** is made from crude cumidine and **4 R** from pure ψ-cumidine.

Produced by the action of diazocumene chloride (from ψ-cumidine) on R-salt. Properties as above; colour of a redder shade than the last.

Literature.—*See* above.

Ponceau 3 R (M.); Dimethylethylbenzeneazo-β-naphthol-3 : 6-disulphonic acid

$$C_2H_5\cdot C_6H_2(CH_3)_2\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH(\beta).$$

Prepared by the action of diazotised ethylxylidine on R-salt.

Literature.—*See* above.

Bordeaux B (H.) (A.) (M.); **Fast Red B** (B.); **Bordeaux BL** (C.); **Bordeaux R extra** (M.); **Cerasine** (P.).; **Archilline 2 B**(Lev.); α-Naphthaleneazo-β-naphthol-3 : 6-disulphonic acid

$$C_{10}H_7\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

Prepared from diazotised α-naphthylamine and R-salt. Solution in water is magenta-red, and in strong sulphuric acid blue becoming magenta-red on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811; A. P. 251164.

Sorbine Red (B.); **Azogrenadine S** (By.); **Lanafuchsine SB** (C.); *p*-Acetylaminobenzeneazo-α-naphthol-3 : 6-disulphonic acid

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on α-naphthol-3 : 6-disulphonic acid. Aqueous solution is currant-red, and, in strong sulphuric acid fiery red. **Lanafuchsine SG** is a closely related dyestuff.

Palatine Scarlet (B.); **Cochineal Scarlet PS** (By.); *m*-Xyleneazo-α-naphthol-3 : 6-disulphonic acid $C_8H_9\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$. Prepared from diazotised *m*-xylidine and α-naphthol-3 : 6-disulphonic acid. Solution in water is scarlet-red and in strong sulphuric acid bluish-red. Closely related dyestuffs are **Palatine Scarlet 3 R** and **4 R** (B.); **Brilliant Cochineal 2 R** and **4 R** (C.).

XL Carmoïsine 6 B (H.).; *m*-Xyleneazodihydroxynaphthalene-3 : 6-disulphonic acid $C_8H_9\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the action of diazotised *m*-xylidine on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromatrope acid).

Eosamine B (A.); Methoxytolueneazo-α-naphthol-3 : 6-disulphonic acid

$$CH_3\cdot O\cdot C_7H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

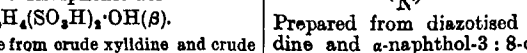
Prepared from diazotised *m*-amino-*p*-cresol methyl ether and α-naphthol-3 : 6-disulphonic acid. Solution in water is bluish-red, and in strong sulphuric acid violet-blue.

Literature.—Chem. Ind. 1896, 19, 8.

Palatine Red (B.); **Naphthorubin** (By.); α-Naphthaleneazo-α-naphthol-3 : 6-disulphonic acid $C_{10}H_7\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$. Prepared from diazotised α-naphthylamine and α-naphthol-3 : 6-disulphonic acid. Bluish-red solution in water, and blue in strong sulphuric acid. A similar colouring matter is **Azo Red A** (C.).

Literature.—E. P. 15716 of 1885; D. R. P. 38281.

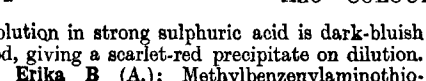
Direct Rose G (K. S.):



Prepared from diazotised dehydrothio-*p*-toluidine and α-naphthol-3 : 8-disulphonic acid (ε-acid). Cherry-red aqueous solution gives a scarlet-red precipitate with hydrochloric acid, and a bluish-red one with sodium hydroxide.

Solution in strong sulphuric acid is dark-bluish red, giving a scarlet-red precipitate on dilution.

Erika B (A.); Methylbenzenylaminothio-xylenolazo-α-naphthol-3 : 6-disulphonic acid



Prepared from diazotised dehydrothio-*m*-xylidine and α-naphthol-3 : 6-disulphonic acid. Solution in water or strong sulphuric acid is red. The various brands of **Geranine** (By.) and **Brilliant Geranine** (By.) are analogously constituted.

Literature.—E. P. 17333 of 1888; D. R. P. 63951; F. P. 194406; A. P. 418657; Schultz, Ber. 1889, 22, 583.

Azo Bordeaux (By.)[1]; Naphthaleneazo-α-naphthol-4 : 8-disulphonic acid

$$C_{10}H_7\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

Prepared by the action of diazotised α-naphthylamine on α-naphthol-4 : 8-disulphonic acid. Magenta-red aqueous solution is not changed by acids or alkalis. Solution in strong sulphuric acid is blue, becoming magenta-red on dilution.

Literature.—E. P. 15775 and 15781 of 1885; D. R. P. 40571, 42304; A. P. 333035.

Azocochineal (By.); Anisoleazo-α-naphthol-4 : 8-disulphonic acid

$$CH_3\cdot O\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

Similarly prepared from diazotised *o*-anisidine. Solution in water and strong sulphuric acid is red.

Literature.—E. P. 15775 of 1885; D. R. P. 40571.

Chromotrope 2 R (M.); **Biebrich Acid Red 4 B** (K.); **XL Carmoisine R** (H.); Benzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $C_6H_5\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Produced from diazotised aniline and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Gives in water a magenta-red, and in strong sulphuric acid a ruby-red solution.

Literature.—E. P. 9258 of 1890; D. R. P. 69095; F. P. 206439; A. P. 458283.

Chromotrope 2 B (M.); *p*-Nitrobenzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the action of diazotised *p*-nitroaniline on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is yellowish-red, and in strong sulphuric acid dark violet.

Literature.—As under Chromotrope 2R.

Victoria Violet 4 BS (M.); *p*-Aminobenzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $NH_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the alkaline reduction of chromotrope 2 B or by eliminating the acetyl group from chromotrope 6 B (*see* below). It gives a dark-violet solution in water, and a bluish-red in strong sulphuric acid. Similar colouring matters are **Victoria Violet 8 BS** (M.) and **Azo Acid Blue B** (M.).

Literature.—E. P. 8270 of 1892; D. R. P. 70885, 73321; F. P. 221363.

Chromotrope 6 B (M.); **XL Fuchsine 6 B** (H.); *p*-Acetylaminobenzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2.$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is violet-red, and in strong sulphuric acid ruby-red

Literature.—D. R. P. 75738.

Chromotrope 10 B (M.); Naphthaleneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid

$$C_{10}H_7\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2.$$

Prepared from diazotised α-naphthylamine and the above acid. Violet solution in water, and greenish-blue in strong sulphuric acid.

Literature.—As under Chromotrope 2 R.

Chromazone Red A (G.); Benzaldehydeazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $CHO\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Produced from diazotised *p*-aminobenzaldehyde and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is red, and in strong sulphuric acid blue.

Literature.—D. R. P. 85233; F. P. 248519.

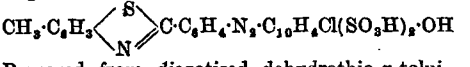
Chromazone Blue R (G.); Phenylethylhydrazone of the preceding colouring matter

$C_6H_5(C_2H_5)N\cdot N:CH\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$.

Prepared either by condensing chromazone red with *as*-phenylethylhydrazone or by the action of diazotised *p*-aminobenzylidenephenylethylhydrazone on 1 : 8-dihydroxy-3 : 6-disulphonic acid. Solution in water is blue-violet, and in strong sulphuric acid blue-red.

Literature as above.

Diamine Rose (C.); **Diamine Pink** (C.); Benzenylaminothiophenolazochloronaphtholdisulphonic acid



Prepared from diazotised dehydrothio-*p*-toluidine and 8-chloro-α-naphthol-3 : 6-disulphonic acid. Magenta-red solution in water, and reddish-violet in strong sulphuric acid.

Literature.—E. P. 1920 of 1894; D. R. P. 79055, 82285, 96768, 99227; F. P. 235271; A. P. 535037.

Fast Acid Fuchsine B (By.); Benzeneazo-1 : 8-aminonaphthol-3 : 6-disulphonic acid

$$C_6H_5\cdot N_2\cdot C_{10}H_3\cdot(SO_3H)_2(OH)\cdot NH_2.$$

Prepared from diazotised aniline and 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) in alkaline solution. Solution in water or strong sulphuric acid is magenta-red.

Literature.—13343 of 1890; D. R. P. 62368, 70031; F. P. 210033.

Toluene Red B (K.); Benzeneazo-1 : 8-aminonaphthol-4 : 6-disulphonic acid. Isomeric with the preceding. Prepared from diazotised aniline and 1 : 8-aminonaphthol-4 : 6-disulphonic acid (K-acid). Solution in water or strong sulphuric acid is magenta-red.

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563383.

Fast Sulphone Violet 5 BS (K. S.) is prepared by combining a diazo- compound with 1 : 8-aminonaphthol-3 : 6- or -4 : 6-disulphonic acid in alkaline solution, and treating the product with *p*-toluenesulphonyl chloride, whereby the amino- group is transformed into the *p*-toluenesulphonylamino- group. Other dyestuffs of the same kind are **Brilliant Sulphone Red B** (K. S.) and **Fast Sulphone Violet 4 R** (K. S.).

Literature.—E. P. 22886 of 1899; D. R. P. 120081.

[1] No longer manufactured under the name 'Buffalo Rubin' by the Schöllkopf Co.

Azorubine S (A.); **Azorubine A** (C.); **Azo Acid Rubine** (C. J.) (D.); **Azo Acid Rubine R** (K.); **Nacarat** (P.); **Fast Red C** (B.); **Carmoisine** (By.); **Carmoisine AS** (Lev.) Sulpho-α-naphthaleneazo-α-naphtholsulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$$

Prepared by the action of diazotised naphthionic acid on α-naphthol-4-sulphonic acid in presence of alkali. Solution gives a red crystalline precipitate with calcium chloride; substance dissolves in strong sulphuric acid with a bluish-violet colour, becoming red on dilution. When used for after-chroming on wool the dyestuff is known as **Azochrome Blue R** (K.).

Literature.—E. P. 2237 and 4237 of 1883; D. R. P. 26012.

Azochrome Blue B (K.); isomeric with the preceding. Prepared from diazotised naphthionic acid and α-naphthol-5 sulphonic acid. Aqueous solution is bluish-red and gives a reddish-brown precipitate with hydrochloric acid. Substance dissolves in strong sulphuric acid with reddish-blue colour.

Fast Red E (B.) (K.); **Fast Red** (Lev.) (A.) (C.J.); Sulpho-α-naphthaleneazo-β-naphtholsulphonic acid $HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH$. Isomeric with the preceding; prepared from diazotised naphthionic acid and Schäffer's β-naphthol-6-sulphonic acid. Aqueous solution claret-red; not precipitated by acids, dissolves in strong sulphuric acid with a violet colour, becoming red on dilution.

Literature.—E. P. 786 of 1878; D. R. P. 5411.

Croceïne Scarlet 3 BX (By.) (K.); **Coccine 2 B** (A.); **Scarlet OOO** (H.). Isomeric with the last; prepared from diazotised naphthionic acid and Bayer's β-naphthol-8-sulphonic acid. Hot solution (concentrated) gives a crystalline magnesium salt on adding magnesium sulphate and allowing to cool; solution in strong sulphuric acid reddish-violet becoming yellowish-red on dilution.

Literature.—E. P. 2031 of 1881; D. R. P. 20402; A. P. 256376.

Double Scarlet Extra S (A.) (Lev.); **Double Brilliant Scarlet 3 R** (By.); **Double Brilliant Scarlet S** (K.); **Brilliant Ponceau 4 R** (By.); **Scarlet PR** (P.). Isomeric with the last; prepared from diazotised β-naphthylamine-6-sulphonic acid (Brönner's), and α-naphthol-4-sulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$$

Aqueous solution gives yellowish-brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour, becoming yellower on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547.

Azofuchsine G (By.); *p*-Sulphobenzeneazodihydroxynaphthalene-4-sulphonic acid

$$HSO_3\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(OH)_2\cdot SO_3H.$$

Prepared from diazotised sulphanilic acid and 1:8-dihydroxynaphthalene-4-sulphonic acid. Solution in water is bluish-red, and in strong sulphuric acid violet. Analogous colours are **Azofuchsine S** and **GN extra** (C.).

Literature.—E. P. 18517 of 1889; D. R. P. 54116; F. P. 203744; A. P. 466841, 468142.

Crumpsall Yellow (Lev.); Disulphonaphthaleneazosalicylic acid

$$C_{10}H_6(SO_3H)_2\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H.$$

Produced by the action of diazotised β-naphthylamine-6:8-disulphonic acid on salicylic acid. Solution in water is yellow, and in strong sulphuric acid, orange-red.

Literature.—E. P. 12145 of 1894; D. R. P. 87483.

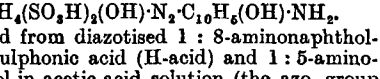
Lanacyl Blue BB (C.); Disulphohydroxynaphthaleneazoaminonaphthol

$$C_{10}H_4(SO_3H)_2(OH)\cdot N_2\cdot C_{10}H_5(OH)\cdot NH_2.$$

Prepared from diazotised 1:8-aminonaphthol-3:6-disulphonic acid (H-acid) and 1:5-aminonaphthol in acetic acid solution (the azo- group attacks the ortho- position relative to the hydroxy- group). Solution in water is reddish or bluish-violet, and in strong sulphuric acid blue. To this group belong also **Lanacyl Blue R** and **Lanacyl Navy Blue B** and **3 B** (C.).

Literature.—E. P. 24134 of 1896; D. R. P. 95190; F. P. 260848.

Rosophenine 10 B (Cl. Co.); **Rosophenine Pink** (Cl. Co.); **Direct Scarlet B** (K.); Sulphobenzenylaminothiocresolazo-α-naphthol-4-sulphonic acid



Prepared from diazotised dehydrothio-*p*-toluidinesulphonic acid and α-naphthol-4-sulphonic acid. Solution in water is crimson-red, and in strong sulphuric acid violet-red.

The corresponding colour from diazotised primuline is called **Rosophenine SG** (Cl. Co.); **Thiazine Red R** (B.) (D. R. P. 48465; F. P. 192628, 196988; A. P. 398990).

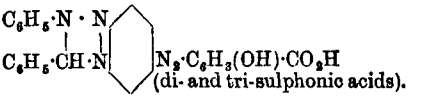
Thiazine Red G (B.). Prepared from diazotised primuline (sulphonic acid) and β-naphthol-6-sulphonic acid. Orange-red aqueous solution gives an orange-red precipitate with hydrochloric acid, and becomes dark with sodium hydroxide. Solution in strong sulphuric acid is blood-red, giving an orange precipitate on dilution.

References as for thiazine red R.

Dianil Yellow 2 R (M.). Prepared by the action of diazotised primuline (sulphonic acid) on 1-*p*-sulphophenyl-3-methyl-5-pyrazolone.

Reactions and references as for dianil yellow R.

Chrome Fast Yellow G (A.); Di-(and tri-)sulphodiphenylphenotriazineazosalicylic acid



Produced from the di-(or tri-)sulphonic acids of the triazine from chrysoïdine and benzaldehyde by diazotisation and combination with salicylic acid. The aqueous solution is orange-yellow, and the solution in strong sulphuric acid is the same.

Literature.—D. R. P. 79425 (compare also D. R. P. 76491 and 78006); Noelting and Wegelin, Ber. 1897, 30, 2595.

3. Trisulphonic Acids.

New Coccine (A.) (Lev.); **Brilliant Scarlet** (C.); **Croceïne Scarlet 4 BX** (K.); **Victoria Scarlet 4 R** (T. M.); **Special Ponceau** (P.); **Cochineal Red A** (B.); Sulpho-α-naphthaleneazo-β-naphthol-6:8-disulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4\cdot(SO_3H)_2\cdot OH.$$

Prepared by the action of diazotised naphthionic

acid on β-naphthol-6 : 8-disulphonic acid (G-salt). Aqueous solution red, not precipitated by acids. Dissolves in strong sulphuric acid with a red colour, becoming yellowish-red on dilution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; A. P. 314938.

Fast Red D (B.); **Azo Acid Rubine 2 B** (D.); **Fast Red EB** (B.); **Cloth Red** (T. M.); **Bordeaux S** (A.) (Lev.); **Amaranth** (M.) (C.). Isomeric with the preceding. Prepared from diazotised naphthionic acid and R-salt.

Literature.—D. R. P. 3229.

Chromotrope 8 B (M.).—*p*-Sulphonaphthalene-azodihydroxynaphthalene-3 : 6-disulphonic acid

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_3(SO_3H)_2(OH)_2.$$

Prepared by the action of diazotised naphthionic acid on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is violet-red, and in strong sulphuric acid indigo-blue. In addition to this and the other 'chromotrope' colours mentioned above, the marks S, SB, SR, 7 B, F B, and F 4 B also appear on the market, but their constitution has not yet been published.

Literature.—E. P. 9258 of 1890; D. R. P. 69095; F. P. 206439; A. P. 458283.

4. Tetrasulphonic Acids.

Ponceau 6 R (M.) (B.); *p*-Sulphonaphthalene-azo-β-naphtholtrisulphonic acid

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_3(SO_3H)_3 \cdot OH.$$

Prepared by the action of diazotised naphthionic acid on β-naphthol-3 : 6 : 8-trisulphonic acid. Solution in water is magenta-red, and in strong sulphuric acid violet.

Literature.—E. P. 2544 of 1882; D. R. P. 22038; F. P. 137109; A. P. 268506.

Heliopurpurine 4 BL (By.); Disulphonaphthaleneazo-α-naphthol-3 : 6-disulphonic acid

$$C_{10}H_5(SO_3H)_2 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$

Prepared from diazotised β-naphthylamine-3 : 6-disulphonic acid and α-naphthol-3 : 6-disulphonic acid. Used exclusively in the manufacture of lakes.

Literature.—Färber-Zeit. 1904, 15, 95.

Heliopurpurine 7 BL (By.) Isomeric with the preceding. Prepared by the action of diazotised β-naphthylamine-1 : 6-disulphonic acid on β-naphthol-3 : 6-disulphonic acid (R-salt). Used only for lakes.

Literature as above.

5. Pentasulphonic Acids.

Heliopurpurine GL (By.); Disulphonaphthaleneazo-β-naphthol-3 : 6 : 8-trisulphonic acid

$$C_{10}H_5(SO_3H)_2 \cdot N_2 \cdot C_{10}H_3(SO_3H)_3 \cdot OH.$$

Prepared from diazotised β-naphthylamine-3 : 6-disulphonic acid and β-naphthol-3 : 6 : 8-trisulphonic acid.

Use and literature as above.

E. Carboxylic Acids of Hydroxyazo- Compounds.[1]

Alizarine Yellow GG (M.); **Chrome Yellow R** (P.); *m*-Nitrobenzeneazosalicylic acid

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared from diazotised *m*-nitroaniline and salicylic acid. The commercial product (the free acid) is a yellow paste, insoluble in water, and giving an orange solution with strong sulphuric acid. The sodium salt is put on the market in the dry state as **Alizarine Yellow GGW** (M.).

Literature.—E. P. 17583 of 1887; D. R. P. 44170; F. P. 187821; A. P. 424019.

Alizarine Yellow R[1] (M.) (C. R.) (By.); **Terracotta** (G.); **Chrome Orange** (P.); **Xanthochromine.** Isomeric with the last. Prepared from diazotised *p*-nitroaniline and salicylic acid. Comes on the market as a brown paste insoluble in water and giving an orange-yellow solution with strong sulphuric acid. This consists of the free acid; the sodium salt (soluble in water with an orange colour) is called **Alizarine Yellow RW** (M.).

Literature.—Meldola, Chem. Soc. Trans. 1885, 47, 666; Bull. Mulhouse, 1892, 198; J. Soc. Chem. Ind. 1890, 9, 53; 1892, 11, 599; J. Soc. Dyers, 1889, 5, 106; E. P. 13920 of 1888.

Persian Yellow (G.); *o*-Nitrotolueneazosalicylic acid $NO_2 \cdot C_7H_6 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$. Prepared by nitrating *p*-tolueneazosalicylic acid (formerly in commerce under the name Flavazol) The commercial product is a 20 p.c. paste soluble in water to a yellow solution, and giving an orange-yellow solution with strong sulphuric acid.

Literature.—E. P. 13920 of 1888; F. P. 193190; A. P. 431297; Ber. 1907, 40, 4207.

Chrome Fast Yellow GG (A.); *o*-Anisoleazosalicylic acid $CH_3 \cdot O \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$. Prepared from diazotised *o*-anisidine and salicylic acid. In commerce as a bright-yellow paste or a yellow powder. Solution in hot water is greenish-yellow, and in strong sulphuric acid yellowish-brown.

Azoalizarine Yellow 6 G (D. H.); **Alizarine Yellow 5 G** (M.); **Tartrachromine GG** (I.); *p*-phenetoleazosalicylic acid

$$C_2H_5 \cdot O \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared from diazotised *p*-phenetidine and salicylic acid. Solution in water is yellowish-brown, and in strong sulphuric acid brown-red.

Diamond Flavine G (By.); *p*-Hydroxydiphenylazosalicylic acid

$$OH \cdot C_{12}H_8 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared by boiling the intermediate product from tetrazotised benzidine and one molecule of salicylic acid. In commerce as a yellowish-brown paste or powder which dissolves in water only after the addition of sodium acetate. Solution in strong sulphuric acid is blood-red.

Literature.—E. P. 11663 of 1891; D. R. P. 60373; F. P. 214756.

Diamond Yellow G (By.); *m*-Carboxybenzeneazosalicylic acid

$$CO_2H \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared from diazotised *m*-aminobenzoic acid and salicylic acid. A greyish-yellow paste soluble in water (with addition of sodium acetate or carbonate) with a yellow colour. Gives a reddish-yellow solution with strong sulphuric acid.

Literature.—E. P. 8299 of 1889; D. R. P. 58271; F. P. 198521 (addition); A. P. 502368, 502369.

Diamond Yellow R (By.). Isomeric with the preceding. Prepared from *o*-aminobenzoic acid and salicylic acid. A brown paste soluble in

[1] Carboxylic acids containing also sulphonic acid groups are described under the corresponding sulphonic or disulphonic) acids.

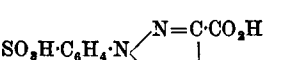
[1] **Meta Chrome Orange R double** (A.) is probably identical with this.

water (in presence of alkalis), with a yellow colour. Solution in strong sulphuric acid is reddish-yellow.

Literature as for the preceding colour.

F. Unclassified Monoazo- Colouring Matters.

Tartrazine (B.) (I.) (H.); **Hydrazine Yellow** (O.); Benzeneazopyrazolonecarboxydisulphonic acid



Prepared (1) by the action of phenylhydrazinesulphonic acid on dihydroxytartaric acid; or (2) by the action of phenylhydrazinesulphonic acid on oxalacetic ester, coupling the product with diazotised sulphanilic acid and hydrolysing. Solution in water or strong sulphuric acid is yellow.

Literature.—E. P. 9858 of 1885; 5693 of 1893; 765 of 1897; D. R. P. 34294; F. P. 169964; A. P. 324630; Ziegler and Locher, Ber. 1887; 20, 834; Anschütz, Annalen, 1897, 294, 219; 1899, 306, 1; Gnehm and Benda, Annalen, 1898, 299, 100; Bernthsen, Chem. Zeit. 1898, 22, 456.

Hydrazine Yellow SO (O.) is probably a nitrotartrazine (D. P. 109914).

III. Disazo- Compounds.[1]

A. Primary Disazo- Colouring Matters.[2]

Leather Brown (O.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(NH_2)_2 \cdot N_2 \cdot C_6H_4 \cdot NH_2$.

Prepared by combining 2 mols. of *p*-diazoacetanilide with 1 mol. of *m*-phenylenediamine, and heating the product with strong hydrochloric acid. Commercial product is the monohydrochloride or the zinc chloride double salt. The brown aqueous solution becomes yellower on adding hydrochloric acid, and gives a brown precipitate with sodium hydroxide. The substance gives a brown solution in strong sulphuric acid, which becomes yellowish-brown on dilution.

Literature.—E. P. 11218 of 1891; D. R. P. 67429; A. P. 462414.

Terra Cotta F (G.):

$P^3 \cdot N_2 \cdot C_6H_2(NH_2)_2 \cdot N_2 \cdot C_{10}H_6 \cdot SO_3H$.

Prepared by combining first diazotised naphthionic acid and secondly diazotised primuline with *m*-phenylenediamine. Solution in water is brown, giving a brown precipitate with hydrochloric acid. Strong sulphuric acid dissolves colour to a reddish-violet solution, giving a brown precipitate on dilution.

Literature.—E. P. 1888 of 1890; F. P. 203439; A. P. 440288.

Cotton Orange R (B.):

$P^3 \cdot N_2 \cdot C_6(NH_2)_2(SO_3H)_2 \cdot N_2 \cdot C_6H_4 \cdot SO_3H$.[4]

Prepared by combining first diazotised primuline and secondly diazotised metanilic acid with *m*-phenylenediaminedisulphonic acid. The orange-red aqueous solution gives a reddish precipitate with hydrochloric acid. Solution in strong sulphuric acid is bright red, precipitating on dilution.

Literature.—E. P. 21753 of 1893; D. R. P. 76118; F. P. 231694; A. P. 524261.

Resorcin Brown (A.) (K.):

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot N_2 \cdot C_8H_9$.

Diazoxylene chloride is combined with resorcin yellow (p. 368). Aqueous solution gives a brown precipitate with acids. Dissolves in strong sulphuric acid with a brown colour.

Literature.—D. R. P. 18862; A. P. 269359.

Fast Brown G (T. M.); **Acid Brown** (D.) (P.).

$(HSO_3 \cdot C_6H_4 \cdot N_2)_2C_{10}H_5 \cdot OH(\alpha)$.

Prepared by the action of diazotised sulphanilic acid (2 mols.) on α-naphthol (1 mol.). Aqueous solution red-brown; violet precipitate with dilute acid. Strong sulphuric acid solution violet, becoming yellowish-brown on dilution.

Literature.—Krohn, Ber. 1888, 21, 3241.

Fast Brown (By.):

$(HSO_3 \cdot C_{10}H_6 \cdot N_2)_2C_6H_2(OH)_2$.

Prepared by the action of diazotised naphthionic acid (2 mols.) on resorcinol (1 mol.). Brown aqueous solution gives a readily soluble precipitate with hydrochloric acid, and becomes cherry red with sodium hydroxide. Solution in strong sulphuric acid is currant-red.

Literature.—D. R. P. 18862.

Palatine Black (B.); **Wool Black 4 B** and **6 B** (A.):

$HSO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_3(SO_3H)(OH)(NH_2) \cdot N_2 \cdot C_{10}H_7$

Prepared by the action of diazotised sulphanilic acid (1 mol.) on 1 : 8-aminonaphthol-4-sulphonic acid in acid solution, and treating the product in alkaline solution with diazotised α-naphthylamine (1 mol.) in alkaline solution. Dark-blue aqueous solution becomes bluish-green with hydrochloric acid and pure blue with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a dark-blue precipitate on dilution.

Literature.—E. P. 7713 of 1891; D. R. P. 91855; F. P. 213232; A. P. 590088.

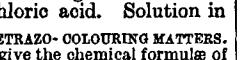
Naphthol Blue Black (C.); **Naphthol Black 12 B** (C.); **Wool Black 6 G extra conc.** (T. M.); **Naphthalene Black 10 B** (P.); **Blue Black NB** (K.); **Coomassie Blue Black** (Lev.):

$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_2(SO_3H)_2(OH)(NH_2) \cdot N_2 \cdot C_6H_5$

Prepared by the action of diazotised *p*-nitroaniline (1 mol.) on 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) in acid solution, and treating the product in alkaline solution with diazotised aniline. The dark-blue aqueous solution gives a blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is green, giving a blue precipitate on dilution.

Literature.—E. P. 6972 of 1891; D. R. P. 65651; F. P. fourth addition to 201770; A. P. 480326.

Chrome Patent Green NC (K.)



Prepared by the action of diazotised aniline (1 mol.) and diazotised picramic acid (1 mol.) on 1 : 8-aminonaphthol-4 : 6-disulphonic acid.

Literature.—D. R. P. 110711; F. P. 291316.

Blue Black N (K.)

$(NO_2 \cdot C_6H_4 \cdot N_2)_2C_{10}H_2(SO_3H)_2(OH) \cdot NH_2$.

[1] *See* also Disazo- and Tetrazo- colouring matters.

[2] It will be sufficient to give the chemical formulæ of these disazo-compounds without giving their names in full.

[3] P = residue of primuline or dehydrothiotoluidine refers to sulphonic acid.

[4] According to Heumann (Die Anilinfarben und ihre Fabrikation) the formula is—

$P \cdot N_2 \cdot C_6H(NH_2)(SO_3H)_2 \cdot NH \cdot N_2 \cdot C_6H_4 \cdot SO_3H$.

Prepared by the action of diazotised *p*-nitroaniline (2 mols.) on 1 : 8-aminonaphthol-4 : 6-disulphonic acid.

Literature.—D. R. P. 108266; F. P. 271070; A. P. 613639.

Supramine Black BR (By.). The special base used in the preparation of this colouring matter is *p*-aminophenyl ether. Two mols (or one of this and one of another base) are diazotised and combined with 1 : 8-aminonaphthol-4 : 6- or 3 : 6-disulphonic acid.

Literature.—F. P. 402546; A. P. 958830.

Janus Yellow R (M.):

$$N(CH_3)_3Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(OH)_2{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2.$$

Prepared by combining diazotised *m*-aminophenyltrimethylammonium chloride with *m*-nitrobenzeneazoresorcinol. Yellowish-brown aqueous solution gives a yellowish-brown precipitate. Solution in strong sulphuric acid is magenta-red, becoming yellow on dilution.

Azidine Fast Scarlet G, 4 BS, 8 BS, 12 BS (C. J.). These dyes are prepared by the action of 2 mols. of a diazo-compound, for example, that from β-naphthylamine on the substance

$$HSO_3{\cdot}C_{10}H_5(OH){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_2(CH_3){\cdot}SO_3H$$
$$\vert$$
$$OH{\cdot}C_{10}H_5(SO_3H){\cdot}NH{\cdot}CO{\cdot}NH$$

Literature.—D. P. (appl.) J. 11718; F. P. 412138; A. P. (appl.) 541843.

Benzo Fast Scarlet GS, 4 BS and **8 BS** (By.). These dyes are obtained by the action of 2 mols. of a diazo-compound on the urea produced by the action of carbonyl chloride on 2 mols. of 5-amino-α-naphthol-3-sulphonic acid (J-acid): *i.e.*

$$HSO_3{\cdot}C_{10}H_5(OH){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_5(OH){\cdot}SO_3H.$$

Literature.—E. P. 3615 of 1900; D. R. P. 122904, 126133, 126801, 128195, 129464, 132511; F. P. 297367; A. P. 653498, 662122, 675629, 675632.

B. Secondary Disazo- Colouring Matters.

Sudan III (A.) (Ib.) (Fi.); **Cerasine Red** (C.); **Cerotine Scarlet R** (C. J.); **Fat Ponceau G** (K.):

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta).$$

Prepared by the action of diazotised aminoazobenzene on β-naphthol. Insoluble in water; dissolves in strong sulphuric acid with a green colour, becoming blue, and finally red and precipitating on dilution.

Literature.—Nietzki, Ber. 1880, 13, 1838; D. R. P. 16483.

Ponceau 5 R (M.) (K.); **Erythrine X** (B.):

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_3{\cdot}OH.$$

Prepared by the action of diazotised aminoazobenzene on β-naphthol-3 : 6 : 8-trisulphonic acid in alkaline solution.

Literature.—E. P. 2544 of 1882; D. R. P. 22038; F. P. 137109; A. P 268507.

Cloth Red G (By.); **Cloth Red R** (D.),

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared by the action of diazotised aminoazobenzene on α-naphthol-4-sulphonic acid in alkaline solution. Dissolves in strong sulphuric acid with a violet colour, giving a brownish-red precipitate on dilution.

Literature.—E. P. 2237 of 1883; D. R. P. 26012.

Croceïne B (Sch.). The disulphonic acid corresponding with the preceding: produced by the action of diazotised aminoazobenzene on α-naphthol-4 : 8-disulphonic acid.

Literature.—E. P. 15775 and 15782 of 1885; D. R. P. 40571; A. P. 333037.

Brilliant Croceïne M (C.) (By.) (M.); **Brilliant Croceïne O** (K.); **Brilliant Croceïne, extra conc.** (T. M.); **Cotton Scarlet** (B.); **Ponceau BO extra** (A.); **Croceïne 3 B** (P.):

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH.$$

Prepared by the action of diazotised aminoazobenzene on β-naphthol-6 : 8-disulphonic acid. Dissolves in strong sulphuric acid with a reddish-violet, becoming first bluer and then red on dilution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; F. P. 159998; A. P. 314939.

Oil Scarlet (M.) (W.); **Red B, Oil soluble, extra conc.** (Remy.); **Cerotine Ponceau 3 B** (C. J.); **Fat Ponceau R** (K.). (*See* also **Fast Azo Garnet**, p. 363.)

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

Prepared from diazotised *o*-aminoazotoluene and β-naphthol. Insoluble in water, but soluble in alcohol or benzene with a bluish-red colour. Strong sulphuric acid gives a blue solution, which yields a red precipitate on dilution.

Cloth Red B (By.) (D.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared by the action of diazotised *o*-aminoazotoluene on α-naphthol-4-sulphonic acid. The red aqueous solution gives a red precipitate with hydrochloric acid, and on adding sodium hydroxide to the solution it becomes violet. The solution in strong sulphuric acid is blackish-blue.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Cloth Red G (O.); **Cloth Red G extra** (By.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\beta).$$

Produced by the action of diazotised aminoazotoluene on β-naphthol-6-sulphonic acid (Schäffer's). Dissolves in water with a red-brown colour giving a similarly coloured precipitate on addition of acid. Dissolves with a blue colour in strong sulphuric acid, giving a brownish-red precipitate on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Cloth Red B (O.) (K.); **Cloth Red O** (M.); **Cloth Red BA** (A.); **Fast Bordeaux O** (M.); **Fast Milling Red B** (Lev.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH(\beta).$$

Prepared by the action of diazotised aminoazotoluene on β-naphthol-3 : 6-disulphonic acid (R-salt). Aqueous solution red, becoming brownish on addition of hydrochloric acid. Dissolves in strong sulphuric acid with a blue colour, giving a brownish-red precipitate on dilution.

Literature as under preceding colour.

Cloth Red 3 G extra (By.); **Cloth Red 3 GA** (A.): $C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_6(SO_3H){\cdot}NH_2$. Prepared by the action of diazotised aminoazotoluene on β-naphthylamine-6-sulphonic acid (Brönner's acid). The red aqueous solution gives with hydrochloric acid a dark reddish-brown precipitate. The solution in strong sulphuric acid is dark greenish-blue, and gives a brownish-red precipitate on dilution.

Bordeaux BX (By.):

$$C_8H_9{\cdot}N_2{\cdot}C_8H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared by the action of diazotised aminoazoxylene on β-naphthol-6-sulphonic acid

(Schäffer's). Solution in water is brownish-red, and gives a brownish-red precipitate with hydrochloric acid or sodium hydroxide. Strong sulphuric acid dissolves colour to a brown solution, which gives a reddish-brown precipitate on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Archil Red A (B.); **Union Fast Claret** (Lev.):

$C_6H_5{\cdot}N_2{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH(\beta)$.

Prepared by the action of diazotised aminoazoxylene on β-naphtholdisulphonic acid (R-salt). Soluble in water with a Bordeaux-red colour; reddish-brown flocculent precipitate on adding dilute acid. Solution in strong sulphuric acid dark blue, giving reddish-brown precipitate on dilution.

Literature.—E. P. 5003 and 5021 of 1879; 536 of 1880; D. R. P. 22010; A. P. 210233, 246221.

Croceïne Scarlet 3 B (By.) (C. J.); **Ponceau 4 RB** (A.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$.

Produced by the action of diazotised aminoazobenzenesulphonic acid on β-naphthol-8-sulphonic acid (Bayer's). Solution not precipitated by alkali; a red precipitate produced by barium chloride, becoming dark-violet and crystalline on boiling. Dissolves in strong sulphuric acid with a deep-blue colour, becoming violet and then red on dilution.

Literature.—E. P. 1225 and 2030 of 1881, 2411 of 1883, 8390 of 1884; D. R. P. 18027; F. P. 142024: A. P. 256380.

Fast Scarlet B (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$.

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on β-naphthol-6-sulphonic acid (Schäffer's). Red solution in water, giving brown precipitate with hydrochloric acid and a red-violet coloration with sodium hydroxide. Solution in strong sulphuric acid is blue, and becomes red on dilution.

Literature.—D. R. P. 16482.

Cloth Scarlet G (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$.

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on β-naphthol. The scarlet solution in water gives a brown precipitate with sodium hydroxide, and becomes yellower on addition of hydrochloric acid when dilute, but in concentrated solutions a light-red precipitate is produced. The solution in strong sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Milling Orange (D.):

$HSO_3\,C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$.

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on salicylic acid. Orange-red solution in water, giving greyish-yellow precipitate with hydrochloric acid, and a dark-red solution and precipitate with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a greyish-yellow precipitate on dilution.

Biebrich Scarlet; **Ponceau 3 RB** (A.); **New Red L** (K.); **Imperial Scarlet** (By.); **Ponceau B** (M.); **Fast Ponceau B** (B.); **Double Scarlet** (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$.

Prepared from diazotised aminoazobenzenedisulphonic acid and β-naphthol. Solution not precipitated by alkali; a brown flocculent precipitate by dilute acids. Dissolves in strong sulphuric acid with a green colour, becoming first blue and finally brown and precipitating on dilution.

Literature.—E. P. 5003 of 1879, 529 of 1880; D. R. P. 16482, 16483; A. P. 224927, 224928; Nietzki, Ber. 1880, 13, 800, 1838; Miller, *ibid.* 542, 803, 980.

Croceïne Scarlet O extra (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_4(SO_3H){\cdot}OH$.

Prepared by the action of diazotised aminoazobenzenedisulphonic acid on β-naphthol-8-sulphonic acid. The yellowish-red aqueous solution gives a violet coloration with hydrochloric acid or sodium hydroxide. The solution in strong sulphuric acid is blue, becoming yellowish-red on dilution.

Fast Ponceau 2 B (B.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$

Prepared by the action of diazotised aminoazobenzenedisulphonic acid on β-naphthol-3 : 6-disulphonic acid (R-salt). Dissolves in strong sulphuric acid with a blue colour, becoming orange-red on dilution.

Literature.—Miller, Ber. 1880, 13, 542, 803; Nietzki, *ibid.* 980, 1838.

Wool Black (A.) (B.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_7H_7$.

Prepared by the action of diazotised aminoazobenzenedisulphonic acid on *p*-tolyl-β-naphthylamine.[1] Aqueous solution gives a violet precipitate with acids. Dissolves with a blue colour in strong sulphuric acid, giving a brown precipitate on dilution, and decomposing on boiling with the formation of Acid Yellow and tolunaphthazine.

Literature.—E. P. 9754 of 1886; D. R. P. 38425; A. P. 354746.

Croceïne Scarlet 7 B; **Ponceau 6 RB** (A.); **Croceïne Scarlet 8 B** (K.) (By.):

$HSO_3{\cdot}C_7H_6{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\beta)$.

Prepared by the action of diazotised aminoazotoluenesulphonic acid on β-naphthol-8-sulphonic acid (Bayer's) in presence of alkali. Resembles croceïne scarlet 3 B in general properties; gives a crystalline magnesium salt on adding magnesium sulphate to hot concentrated solution and allowing to cool. Dissolves with a blue colour in strong sulphuric acid, becoming red on dilution.

Literature as for croceïne scarlet 3 B; and A. P. 256375.

Orseilline 2 B (By.). Prepared by the action of diazotised aminoazotoluenesulphonic acid on α-naphthol-4-sulphonic acid. Dissolves with a blue colour in strong sulphuric acid, becoming red on dilution.

Literature.—E. P. 2237 and 4237 of 1883; D. R. P. 26012.

Bordeaux G (By.). Prepared by the action of diazotised aminoazotoluenemonosulphonic acid on β-naphthol-6-sulphonic acid (Schäffer's).

Literature.—E. P. 5003 of 1879.

Bordeaux BX (By.).—

$HSO_3{\cdot}C_8H_8{\cdot}N_2{\cdot}C_8H_7(SO_3H){\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$

[1] Prepared by heating β-naphthol with paratoluidine and dry calcium chloride:

$C_{10}H_7{\cdot}OH+C_7H_7{\cdot}NH_2,HCl = C_{10}H_7{\cdot}NH{\cdot}C_7H_7+H_2O+HCl$

(Friedländer, Ber. 1883, 16, 2078).

Prepared by the action of diazotised aminoazoxylenedisulphonic acid on β-naphthol-6-sulphonic acid (Schäffer's). Red aqueous solution giving reddish-brown precipitate with hydrochloric acid and becoming browner with sodium hydroxide. Strong sulphuric acid gives a dark-green solution which turns blue and finally gives a brownish-red precipitate on dilution.

Literature.—E. P. 5003 of 1879.

Eriochrome Verdone A (G.):

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_7H_5(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

Sulphanilic acid is diazotised and combined with *m*-amino-*p*-cresol and the product is diazotised and combined with β-naphthol. The violet aqueous solution becomes claret-red with hydrochloric acid, and blue-green with sodium hydroxide. The solution in strong sulphuric acid is green, giving a brown-red precipitate on dilution. Wool is dyed in claret-red shades from an acid-bath and on chroming becomes blue-green.

Literature.—E. P. 13904 of 1909; D. R. P. 201377; F. P. 404536.

Janus Red (M.):

$N(CH_3)_3Cl \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CH_3) \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

Prepared by diazotising *m*-aminophenyltrimethylammonium chloride, combining with *m*-toluidine, diazotising the product and combining with β-naphthol. The red aqueous solution gives a brownish-red precipitate with hydrochloric acid and a bluish-violet precipitate with sodium hydroxide. The solution in strong sulphuric acid is green, and gives a red precipitate on dilution.

Literature.—D. R. P. 93499.

Nyanza Black B (A.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)(NH_2) \cdot OH$.

Prepared by the action of diazotised *p*-aminobenzeneazo-α-naphthylamine (only one amino-group is diazotised)[1] on 7-amino-α-naphthol-3-sulphonic acid (γ-acid). Solution is dark-violet and gives violet precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is blue, and gives a violet precipitate on dilution. The colouring matter itself produces only indifferent shades, but when diazotised and developed on the fibre fast shades are obtained. When developed with *m*-tolylenediamine, a brown-black is obtained, and with β-naphthol a navy-blue.

Literature.—E. P. 277 and 6630 of 1892; D. R. P. 72394; F. P. 221378; A. P. 491410, 511688, 512167.

Coomassie Wool Black R (Lev.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$.

Prepared by the action of diazotised *p*-acetylaminobenzeneazo-α-naphthylamine on β-naphthol-6-sulphonic acid (Schäffer's), and hydrolysing the product. The dark-violet solution gives a precipitate with hydrochloric acid. The solution in strong sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 24980 of 1899; D. R. P. 122457; A. P. (appl.) 1764 of 1900.

Coomassie Wool Black S (Lev.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH$.

Prepared as the preceding dyestuff, the final component being β-naphthol-3 : 6-disulphonic acid (R-salt). The blue-black aqueous solution becomes redder with hydrochloric acid. The solution in strong sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 24980 of 1899; D. R. P. 122457; A. P. (appl.) 1763 of 1900.

Granite Black (A.):

$OH \cdot C_6H_2(NO_2)_2 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

Picramic acid is diazotised and combined with α-naphthylamine-6-(or 7)-sulphuric acid, and the product is diazotised and combined with β-naphthol. The dark-violet blue aqueous solution gives a dark greenish-blue precipitate with sodium hydroxide, and a dark violet-blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is blackish-violet.

Literature.—E. P. 21437 of 1896; D. R. P. 113241; F. P. 260056; A. P. 583439.

Diaminogen Black (C.):

$NH_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$.

Monoacetyl-1 : 4-naphthylenediamine-7 sulphonic acid is diazotised and combined with α-naphthylamine, the intermediate product diazotised and combined with 7-amino-α-naphthol-3-sulphonic acid (γ-acid), and the product saponified. When diazotised and developed on the fibre a fast black is produced.

Literature.—E. P. 15443 of 1893; D. R. P. 78831; F. P. 232299; A. P. 533463.

Diaminogen Blue BB (C.). Prepared as the preceding, but the end component is β-naphthol-6-sulphonic acid (Schäffer's).

Literature as above.

Diaminogen Blue G (C.). Prepared as above, the end-component being β-naphthol-3 : 6-disulphonic acid (R-salt).

Literature as above.

Diazo Indigo Blue is an analogous product.

Zambesi Sky Blue 4 B (A.). Prepared from diazotised monoacetyl-3 : 6-diaminocresyl methyl ether combined with α-naphthylamine,[1] the intermediate product being diazotised and combined with β-naphthol-6-sulphonic acid and the end-product saponified. The reddish-violet aqueous solution becomes redder with hydrochloric acid and bluer with sodium hydroxide. The solution in strong sulphuric acid is blue and becomes violet-red on dilution.

Literature.—E. P. 2188 of 1901; D. R. P. 126172.

Victoria Black B (By.):

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H) \cdot OH$.

Prepared by the action of diazotised *p*-sulphobenzeneazo-α-naphthylamine on 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The dark reddish-violet aqueous solution gives with hydrochloric acid a Bordeaux-red precipitate, and with sodium hydroxide becomes dark-blue violet. The solution in strong sulphuric acid is moss-green, changing on dilution to sea-green and then to bluish-red.

Literature.—E. P. 13665 of 1889; D. R. P. 61707, 62945; F. P. 200520; A. P. 466202.

Jet Black R (By.):

$(HSO_3)_2C_6H_3 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot C_6H_5$.

Prepared by the action of diazotised disulphobenzeneazo-α-naphthylamine on phenyl-α-naphthylamine. The bluish-violet aqueous

[1] All the authorities give the above constitution for this colouring matter, but it is generally understood that a benzenoid amino- group is diazotised preferably to a naphthalenoid amino- group.

[1] According to Buntrock (Zeitsch. Farben-Ind. 1902 1, 224). The patents quoted give the 6- or 7-sulphonic acid as intermediate component.

solution gives a bluish-black precipitate with hydrochloric acid, and a soluble violet precipitate with sodium hydroxide. Strong sulphuric acid dissolves the colouring matter to a blue solution, which gives a greenish-blue precipitate on dilution.

Literature.—E. P. 14442 of 1888; D. R. P. 48924; F. P. 193430; A. P. 425885.

Diamond Black F[1] (By.); **Chrome Fast Black B** (I.); **Chrome Deep Black D, extra conc.** (T. M.); **Salicin Black D** (K.):

$CO_2H{\cdot}C_6H_3(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$

Aminosalicylic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with α-naphthol-4-sulphonic acid. Bluish-violet solution gives violet precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in strong sulphuric acid is greenish, giving a violet precipitate on dilution. Similar dyestuffs are **Era Blacks J, F, NG, B** and **R** (Lev.).

Literature.—E. P. 8299 of 1899; D. R. P. 51504; F. P. 198521; A. P. 438438.

Chrome Black I (H.):

$$CO_2H{\cdot}C_6H_2(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5{\cdot}OH$$
$$\quad\quad|\quad\quad\quad\quad\quad\quad\quad\quad|$$
$$\quad SO_3H\quad\quad\quad\quad\quad\quad SO_3H$$

Prepared as above, except that the starting material is the sulphonic acid of aminosalicylic acid. The red-violet aqueous solution becomes crimson with hydrochloric acid, and blue with sodium hydroxide. The solution in strong sulphuric acid is bluish-green, becoming violet on dilution.

Literature.—E. P. 2468 of 1899; D. R. P. 123115; F. P. 293923.

Nerol B (A.):

$$C_6H_5{\cdot}NH{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4{\cdot}OH$$
$$\quad\quad|\quad\quad\quad\quad\quad\quad\quad\quad|$$
$$\quad SO_3H\quad\quad\quad\quad\quad\quad SO_3H$$

p-Aminodiphenylamine-*o*-sulphonic acid is diazotised and combined with α-naphthylamine, and the intermediate product is diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). Dark violet-blue solution in water gives a blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is dark-blue violet, giving a blue-violet precipitate on dilution.

Literature.—E. P. 24527 of 1897; D. R. P. 101274; F. P. 271609.

Nerol 2 B (A.). Prepared as the preceding, except that the last component is α-naphthol-4-sulphonic acid.

Properties and literature as above.

Diamond Green (By.):

$$C_6H_3(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2{\cdot}$$
$$\quad|$$
$$CO_2H{\cdot}$$

Prepared by diazotising aminosalicylic acid and combining with α-naphthylamine, the intermediate product being diazotised and combined with 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The blackish-violet aqueous solution gives a dark reddish-violet precipitate with hydrochloric acid, and becomes dark blue with sodium hydroxide. The solution in strong sulphuric acid is bluish-green, becoming greenish-blue, and finally giving a blackish-violet precipitate on dilution.

[1] The yearly production of this important colouring matter is about 2,000,000 kilos.

Literature.—As for Diamond Black F; and D. R. P. 62003.

Naphthylamine Black D (C.) (K.); **Deep Black D, conc.** (T. M.); **Naphthalene Black A** (P.); **Coomassie Wool Black D** (Lev.):

$(HSO_3)_2C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2.$

α-Naphthylamine-4 : 7-disulphonic acid is diazotised and combined with α-naphthylamine, and the intermediate product diazotised and combined with α-naphthylamine. The violet-black aqueous solution gives a black precipitate with hydrochloric acid. The solution in strong sulphuric acid is bluish-black and on dilution becomes green, and finally gives a black precipitate.

Literature.—E. P. 18425 of 1888; D. R. P. 50907; F. P. 170342; A. P. 412440.

Naphthylamine Black 4 B (C.) is a mixture of Naphthol blue black and the preceding colouring matter.

Naphthyl Blue Black N (C.).—Disulphonaphthaleneazo-α-naphthylamine ethyl ether is diazotised and combined with α-naphthylamine. The dark-violet aqueous solution turns blue and gives a blackish-blue precipitate with hydrochloric acid, and becomes blue and precipitates with sodium hydroxide. The solution in strong sulphuric acid is dark blue, which on dilution becomes blue, and finally bluish-violet.

Literature.—Chem. Ind. 1896, 19, 548.

Anthracite Black B (C.); **Phenylene Black** (P.):

$(HSO_3)_2C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_3(NH{\cdot}C_6H_5)_2.$

α-Naphthylamine-3 : 6-(4 : 7-in the case of the latter dye)-disulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with diphenyl-*m*-phenylenediamine. The dull-violet aqueous solution gives a violet precipitate with hydrochloric acid. The solution in strong sulphuric acid is black, giving a greenish-black precipitate on dilution.

Literature.—E. P. 4825 and 7977 of 1889; D. R. P. 52616, 61202; F. P. 196793, 197963; A. P. 502912.

Naphthol Black B (C.); **Brilliant Black B** (B.); **Naphthol Black OPAS** (Lev.).

$(HSO_3)_2C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH.$

β-Naphthylamine-6 : 8-disulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). The violet aqueous solution gives with hydrochloric acid a reddish-violet and with sodium hydroxide a blue precipitate. The solution in strong sulphuric acid is green, becoming bluer on dilution, and then giving a reddish-violet precipitate.

Literature.—E. P. 9214 of 1885; D. R. P. 39029; F. P. 170342; A. P. 345901.

Naphthol Black 2 B (Lev.) is prepared as the preceding, but starting with α-naphthylamine-3 : 6-disulphonic acid.

Blue Black B (B.); **Azo Black O** (M.):

$SO_3H{\cdot}C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H){\cdot}OH,$

β-naphthylamine-8-sulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with β-naphtholdisulphonic acid (R-salt). Aqueous solution gives a bluish precipitate with acids

and sodium hydroxide. Solution in strong sulphuric acid bluish-green, becoming blue, and finally precipitating on dilution.

Naphthol Black 6 B (C.) (D.) (K.); **Acid Black 6 B** (H.); **Brilliant Black BL** and **BD** (B.); **Naphthalene Black 5 B** (P.) is prepared by the action of diazotised disulphonaphthaleneazo-α-naphthylamine on β-naphtholdisulphonic acid (R-salt). Aqueous solution dark violet, becoming dark blue with acid or alkali; dissolves in strong sulphuric acid with a dark-green colour, becoming blue on dilution.

Literature.—E. P. 9214 of 1885; D. R. P. 39029; F. P. 170342; A. P. 345901.

Biebrich Patent Black BO (K.):

$$(HSO_3)_2C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH.$$
$$\quad\quad\quad

The orange-red aqueous solution gives a bluish-violet precipitate with hydrochloric acid. The solution in strong sulphuric acid is magenta-red, giving a bluish-violet precipitate on dilution.

Literature.—As above.

Benzo Fast Pink 2 BL (By.):

$$CO\begin{<}C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2\\ C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2\end{.}$$

Prepared from tetrazotised di-*p*-aminodiphenylcarbamidedisulphonic acid and 7-amino-α-naphthol-3-sulphonic acid (γ-acid; 2 mols.). The red aqueous solution becomes reddish-violet with hydrochloric acid and yellower with sodium hydroxide. The solution in strong sulphuric acid is blue, giving an almost black precipitate on dilution.

Literature.—D. R. P. 129388, 131513; Zeitsch. Farben.-Ind. 1902, 1, 192; Chem. Zeit. 1902, 26, 485.

Bismarck Brown (most firms); **Manchester Brown**; **Phenylene Brown**; **Vesuvine**; **Leather Brown**; **Cinnamon Brown**; **English Brown**; **Brown A** (P.):

$$(NH_2)_2C_6H_3\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NH_2)_2.$$

Prepared by adding a solution of 42·5 kilos. of sodium nitrite and 127·5 kilos. of hydrochloric acid to a solution of *m*-phenylenediamine prepared by reducing 250 kilos. of *m*-dinitrobenzene. The commercial product is the hydrochloride. The aqueous solution gives a brown precipitate with sodium hydroxide. The solution in strong sulphuric acid is brown, becoming red on dilution.

Literature.—E. P. 3307 of 1863; Zeitsch. f. Chem. 1867, 3, 287; Ber. 1897, 30, 2111, 2203, 2899.

Azo- Alizarine Bordeaux W (D. H.):

$$CO_2H\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$$

p-Aminoacetanilide is diazotised and combined with salicylic acid, the product hydrolysed and diazotised and combined with α-naphthol-4-sulphonic acid. The aqueous solution is red, and that in strong sulphuric acid is blue.

Literature.—E. P. 1033 of 1899; F. P. 284775; A. P. 631089.

Azo- Alizarine Black (D. H.). Prepared as the preceding, except that the end-component is 1 : 8-dihydroxynaphthalene-3 : 6-di-(or 4-mono)-sulphonic acid. The aqueous solution is violet, and that in strong sulphuric acid blue.

Literature.—E. P. 1033 of 1899; F. P. 284775; A. P. 640010, 628721.

Violet Black (B.):

$$NH_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$$

p-Aminoacetanilide is diazotised and combined with 1 mol. of α-naphthol-4-sulphonic acid. The acetyl- group is then removed by heating with acid or alkali, and the amino- compound is diazotised and combined with 1 mol. of α-naphthylamine. Aqueous solution brownish-red, giving violet precipitate with mineral acids and reddish-violet coloration with acetic acid or with sodium hydroxide; blue solution in strong sulphuric acid giving violet precipitate on dilution.

Literature.—D. R. P. 42814.

Ingrain Black C (H.):

$$HSO_3\cdot C_6H_5(NH_2)\cdot N_2\cdot C_6H_4\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2.$$

p-Aminoacetanilide is diazotised and combined with α-naphthylamine-6-(or 7)-sulphonic acid (Cleve's acid), the product saponified, diazotised and combined with 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid).

Acid Alizarine Black SE (M.); **Palatine Chrome Black F** (B.):

$$HSO_3\cdot C_6H_2(OH)(N_2\cdot C_{10}H_6\cdot OH)_2.$$

Prepared from tetrazotised 2 : 6-diaminophenol-4-sulphonic acid and β-naphthol (2 mols.). Dark-blue aqueous solution gives a red precipitate with hydrochloric acid and a greenish-blue precipitate with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a red precipitate on dilution.

Literature.—D. R. P. 147880.

Manchester Brown EE (C.); **Bismarck Brown R** (H.) (W.) (I.); **Bismarck Brown 2 R, extra conc.** (T. M.); **Vesuvine B** (B); **Brown N** (P.):

$$(NH_2)_2C_7H_5\cdot N_2\cdot C_7H_6\cdot N_2\cdot C_7H_5(NH_2)_2.$$

Prepared in the same manner as Bismarck brown, but *m*-tolylenediamine is used instead of *m*-phenylenediamine. The reddish-brown aqueous solution becomes yellowish-brown with hydrochloric acid, and gives a light-brown precipitate with sodium hydroxide. The solution in strong sulphuric acid is dark brown, becoming first red and then brown on dilution.

Literature.—Griess, Ber. 1878, 11, 627.

Toluylene Brown G (O.) (By.):

$$HSO_3\cdot C_7H_5\begin{<}N_2\\ N_2\end{>}C_6H_2(NH_2)_2.$$

Prepared by the action of tetrazotised tolylenediaminesulphonic acid ($CH_3 : NH_2 : SO_3H : NH_2$ = 1 : 2 : 4 : 6) on 1 mol. of *m*-phenylenediamine. Solution in water is brown, and in strong sulphuric acid brownish-red.

Literature.—E. P. 17546 of 1892; D. R. P. 65853; A. P. 516380.

Toluylene Yellow (O.). Prepared from the same tetrazo- compound as the preceding, and 2 mols. of 6-nitro-*m*-phenylenediamine in hydrochloric acid solution. The yellowish-brown aqueous solution gives brown precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is brown.

Literature.—E. P. 1331 of 1896; D. R. P. 86940.

Toluylene Orange RR (O.). Prepared from the same tetrazo- compound as before, and 2 mols. of β-naphthylamine. The yellowish-red aqueous solution gives a brownish-red precipitate with hydrochloric acid, and a yellowish-red precipitate with sodium hydroxide. The solution in strong sulphuric acid is bluish-grey.

Literature.—E. P. 17546 of 1892; D. R. P. 70147; A. P. 497032.

Diamine Gold (C.):

$$C_2H_5\cdot O\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot N_2\cdot C_6H_4\cdot OH.$$

Prepared from tetrazotised 1 : 5-naphthylenediamine-3 : 7-disulphonic acid and phenol (2 mols.), the product then being ethylated. The yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid and a yellow precipitate with sodium hydroxide. The solution in strong sulphuric acid is reddish-violet, becoming green and then yellow on dilution.

Literature.—E. P. 15346 of 1890; D. R. P. 61174; F. P. 182063; A. P. 472121.

Naphthylene Violet (C.):

$$NH_2\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot N_2\cdot C_{10}H_6\cdot NH_2.$$

Prepared from the preceding tetrazo- compound and α-naphthylamine (2 mols.). The Bordeaux-red aqueous solution gives a blue precipitate with hydrochloric acid, and a red precipitate with sodium hydroxide. The solution in strong sulphuric acid is blue, and gives a violet precipitate on dilution. The colouring matter is usually diazotised and developed on the fibre or treated on the fibre with nitrous acid, the latter colour being known as **Diamine Cutch**, which is a fast brown shade.

Literature.—E. P. 15346 of 1890; D. R. P. 62075; F. P. 208526; A. P. 464566.

Coomassie Navy Blue (Lev.).—

$(HSO_3)_2C_{10}H_4(OH)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH.$

Prepared by diazotising 1 : 4-naphthylenediamine-2-sulphonic acid (only one amino-group can be diazotised), combining with β-naphthol-3 : 6-disulphonic acid, diazotising the product (the second amino- group can now be diazotised), and combining with β-naphthol. Dark-blue aqueous solution becomes violet with sodium hydroxide. Solution in strong sulphuric acid is blue-green, becoming dark blue on dilution.

Literature.—E. P. 2946 of 1896; D. R. P. 102160; F. P. 256862; A. P. 619194, 639748.

Diphenyl Fast Black [1] (G.):

$$NH\begin{cases}C_7H_6\cdot N_2\cdot C_{10}H_4(OH)(NH_2)\cdot SO_3H\\ C_7H_6\cdot N_2\cdot C_7H_5(NH_2).\end{cases}$$

Prepared from tetrazotised *p*-diaminoditolylamine and 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) and 1 mol. of *m*-tolylenediamine. The violet-black aqueous solution gives with hydrochloric acid a bluish-black precipitate, and with sodium hydroxide a black precipitate. The solution in strong sulphuric acid is dark blue, and gives a black precipitate on dilution.

Literature.—E. P. 16582 of 1896; F. P. 258521; A. P. 575904.

Dianthine (Claus & Co.); **St. Denis Red** (P.); **Rosophenine 4 B** (Cl. Co.); **Rosanol 4 B** (K.):

$$O\begin{cases}N\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ \\ N\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.\end{cases}$$

Prepared from tetrazotised diaminoazoxytoluene and α-naphthol-4-sulphonic acid (2 mols.). The red aqueous solution gives red precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is red, and gives a red precipitate on dilution.

Literature.—E. P. 9315 of 1887, 5736 of 1890; D. R. P. 44045; F. P. 184549; Compt. rend. 1901, 132, 985.

Congo Orange G (A.):

$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_4\cdot O\cdot C_2H_5\\ |\\ C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2.\end{array}$$

Prepared from tetrazotised benzidine [2] and 1 mol. of β-naphthylamine-3 : 6-disulphonic acid, and 1 mol. of phenol, the product being ethylated. The orange-yellow aqueous solution gives a brown precipitate with hydrochloric acid. The solution in strong sulphuric acid is blue, becoming reddish-violet on dilution, and finally giving a brown precipitate. The corresponding colouring matter from tolidine is **Congo Orange R** (A.).

Literature.—E. P. 17957 of 1889; D. R. P. 52328.

Pyramidol Brown BG (P. L.):

$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(OH)_2\\ |\\ C_6H_4\cdot N_2\cdot C_6H_3(OH)_2.\end{array}$$

Prepared from tetrazotised benzidine and resorcinol (2 mols.). The orange-brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes Bordeaux-red with sodium hydroxide. The solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution. Cotton dyed red with this colouring matter is converted into a deep brown when treated with a diazo- compound on the fibre.

Chrysamine G (By.) (A.) (Lev.) (H.); **Azidine Yellow G** (C. J.):

$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H\\ |\\ C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H.\end{array}$$

Prepared by the action of tetrazotised benzidine on salicylic acid (2 mols.) in alkaline solution. Used for dyeing cotton goods yellow directly from a soap-bath. Aqueous solution orange, becoming redder on addition of sodium hydroxide; orange flocculent precipitate, with dilute sulphuric acid. Soluble in strong sulphuric acid, with a magenta-red colour, becoming orange and precipitating on dilution. The homologue from tetrazoditolyl is **Chrysamine R.**

Literature.—E. P. 9162 and 9606 of 1884; D. R. P. 31658; A. P. 329638.

Cresotine Yellow G (A.) (By.) (O.):

$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH\\ |\\ C_6H_4\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH.\end{array}$$

Prepared from tetrazotised benzidine and hydroxytoluic acid (OH : CH_3 : CO_2H = 1 : 2 : 6). Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid and becomes yellowish-red with sodium hydroxide. Solution in strong sulphuric acid is reddish-violet, precipitating on dilution. The corresponding colouring matter from tolidine is **Cresotine Yellow R** (A.) (By.) (O.); **Azidine Yellow R** (C. J.).

Literature.—E. P. 7997 of 1888; A. P. 394841.

Cloth Orange (By.):

$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH\\ |\\ C_6H_4\cdot N_2\cdot C_6H_3(OH)_2.\end{array}$$

Prepared from diazotised benzidine and 1 mol. each of salicylic acid and resorcinol. Yellowish-brown solution gives brown precipitate with hydrochloric acid, and becomes red with sodium hydroxide. Solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution.

Literature.—E. P. 2213 of 1886 and 6687 of 1887; D. R. P. 44797.

Cloth Brown R (By.):

$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH\\ |\\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.\end{array}$$

[1] **Diamine Deep Black** (C.) is derived from *p*-diaminodiphenylamine; **Pluto Black** (By.) also belongs to the same class.

[2] Benzidine or *p*-diaminodiphenyl is prepared by reducing nitrobenzene with zinc-dust and alkali to hydrazobenzene and converting this by means of acids into benzidine. The homologues of benzidine are prepared in a similar manner.

Prepared from tetrazotised benzidine, and 1 mol. each of salicylic acid and α-naphthol-4-sulphonic acid. Reddish-brown aqueous solution gives a brown precipitate with hydrochloric acid. Solution in strong sulphuric acid is bluish-violet, giving a reddish-brown precipitate on dilution.

Literature.—As for the preceding.

Cloth Brown G (By.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(OH)_2.$$

Prepared from tetrazotised benzidine and 1 mol. of salicylic acid and 1 mol. of 2 : 7-dihydroxynaphthalene (the latter combined in weak acetic acid solution). The brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes reddish-brown with sodium hydroxide. The solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution.

Literature.—As for **Cloth Brown R.**

Benzo Orange R (By.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and naphthionic acid. The orange-yellow aqueous solution becomes reddish-violet with hydrochloric acid, and gives a reddish-yellow precipitate with sodium hydroxide. Solution in strong sulphuric acid is violet-blue, giving a greyish-violet precipitate on dilution.

Literature.—E. P. 2213 of 1886; D. R. P. 44797; A. P. 447303.

Diamine Fast Red F (C.); **Dianol Fast Red F** (Lev.) **Azidine Fast Red F** (C. J.); **Oxamine Fast Red F** (B.); **Naphthamine Red H** (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH.$$

Prepared from tetrazotised benzidine and 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) combined in acid solution, and 1 mol. of salicylic acid. Red aqueous solution gives a brown precipitate with hydrochloric acid. The solution in strong sulphuric acid is reddish-blue, and gives a brown precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857; F. P. 201770.

Crumpsall Direct Fast Red R (Lev.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH.$$

Prepared from tetrazotised benzidine and 1 mol. each of β-naphthol-3 : 6-disulphonic acid (R-salt) and salicylic acid.

Diamine Brown M (C.); **Chlorazol Brown M** (H.); **Renol Brown MB, conc.** (T. M.); **Azidine Brown M** (C. J.); **Naphthamine Brown H** (K.); **Crumpsall Direct Fast Brown B** (Lev.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-amino-α-naphthol-3-sulphonic acid (γ-acid); the latter being combined in alkaline solution. The reddish-brown aqueous solution gives a brown precipitate with hydrochloric acid and a reddish-brown precipitate with sodium hydroxide. The solution in strong sulphuric acid is violet, changing to brown on dilution.

Literature.—D. R. P. 57857; F. P. 201770.

Diphenyl Brown BN (G.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}N(CH_3)_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-dimethylamino-α-naphthol-3-sulphonic acid. [The corresponding colouring matter from the monomethylamino-compound is **Diphenyl Brown RN** (G.).] The dark-brown solution gives a red precipitate with hydrochloric acid. The solution in strong sulphuric acid is bluish-violet, giving a red precipitate on dilution. When tolidine is used instead of benzidine, **Diphenyl Brown 3 GN** is obtained.

Literature.—E. P. 2771 of 1896; D. R. P. 103149; F. P. 250697; A. P. 567413.

Diamine Brown B (C.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH{\cdot}C_6H_5.$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-phenylamino-α-naphthol-3-sulphonic acid. The dark-brown aqueous solution gives a Bordeaux-red precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a brown precipitate on dilution.

Oxamine Maroon (B.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared by combining tetrazotised benzidine with 1 mol. of 5-amino-α-naphthol-3-sulphonic acid in alkaline solution, and adding 1 mol. of salicylic acid to the product. The ruby-red aqueous solution does not change with acids or alkalis. The solution in strong sulphuric acid is dark violet, changing to wine-red on dilution.

Literature.—E. P. 2370 of 1893; D. R. P. 82572; F. P. 229263.

Oxamine Red (B.). Isomeric with the preceding. 6-Amino-α-naphthol-3-sulphonic acid is used instead of the 5-amino- acid. The red aqueous solution is not changed by hydrochloric acid, but becomes slightly more violet with sodium hydroxide. The solution in strong sulphuric acid is blue, changing to wine-red on dilution.

Literature.—E. P. 2622614 of 1893; D. R. P. 93276; F. P. 227892; A. P. 555359.

Wool Red G (B.):

$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of phenol-*o*-sulphonic acid and 7-amino-α-naphthol-3-sulphonic acid (γ-acid) the latter being combined in acid solution. The red aqueous solution gives a brown precipitate with hydrochloric acid, and becomes dark red with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a brown precipitate on dilution.

Literature.—D. R. P. appl. 29649 of 1901; F. P. 313533.

Diamine Scarlet B (C.); **Dianil Ponceau G** (M.)[1]:

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_6H_4\cdot O\cdot C_2H_5 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH. \end{array}$$

Tetrazotised benzidine is combined first with 1 mol. of β-naphthylamine-6 : 8-disulphonic acid, then with 1 mol. of phenol and the product is ethylated. The red aqueous solution becomes brownish-red with hydrochloric acid. The solution in strong sulphuric acid is violet, becoming brown on dilution.

Literature.—E. P. 12560 of 1889; D. R. P. 54084; F. P. 200152; A. P. 426345.

Pyramine Orange 2 R (B.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_6H_2(NH_2)_2\cdot NO_2. \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of β-naphthylamine-3 : 6-disulphonic acid and *p*-nitro-*m*-phenylenediamine. The yellow aqueous solution is not changed by acids or alkalis. The solution in strong sulphuric acid is blue, becoming yellowish-red on dilution.

Literature.—E. P. 6827 of 1899; D. R. P. 107731; F. P. 280914; A. P. 631611.

Pyramine Orange 3 G (B.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_6H_2(NH_2)_2\cdot NO_2 \\ | \\ C_6H_4\cdot N_2\cdot C_6H(SO_3H)_2(NH_2)_2. \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of *m*-phenylenediamine-4 : 6-disulphonic acid and *p*-nitro-*m*-phenylenediamine. The yellowish-red aqueous solution is not changed by acids or alkalis. The solution in strong sulphuric acid is yellowish-red, becoming brownish-yellow on dilution.

Literature.—E. P. 18506 of 1898; D. R. P. 105349; F. P. 280914; A. P. 631610.

Congo Red (Lev.) (A.) (By.); **Congo Red R** (H.); **Cosmos Red** (B.); **Cotton Red conc.** (T. M.); **Cotton Red G** (P.); **Cotton Red B** (K):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2. \end{array}$$

Prepared by the action of tetrazotised benzidine on naphthionic acid (2 mols). It can also be obtained by oxidising benzeneazonaphthionic acid with manganese dioxide in sulphuric acid solution (E. P. 6697 of 1895; D. P. 84893; F. P. 248210). The red aqueous solution becomes blue on addition of dilute acids; substance dissolves in strong sulphuric acid with a slaty blue, giving a bluish precipitate on dilution.

Literature.—E. P. 4415 of 1884; D. R. P. 28753; Ber. 1886, 19, 1719.

Diazo Black B (By.). Isomeric with the preceding. Prepared from tetrazotised benzidine and α-naphthylamine-5-sulphonic acid (L-acid; 2 mols.). The violet aqueous solution becomes blue with hydrochloric acid, and gives a blue precipitate with sodium hydroxide. The solution in strong sulphuric acid is blue, remaining blue on dilution. The colouring matter is generally diazotised and developed on the fibre.

[1] **Diamine Scarlet 3 B** (C.); **Dianil Ponceau 2 R** (M.) belongs to the same group, but is bluer.

Congo Rubine (A.) (Lev).; **Azidine Bordeaux** (C. J.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH. \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-8-sulphonic acid and naphthionic acid. The cherry-red aqueous solution gives a blue precipitate with hydrochloric acid and a violet-red one with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—D. R. P. 62659.

Congo Corinth G (A.) (By.); **Cotton Corinth G** (B.); **Dianil Bordeaux G** (M.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2. \end{array}$$

Prepared from tetrazotised benzidine, α-naphthylamine-4-sulphonic acid and α-naphthol-4-sulphonic acid. Aqueous solution red; violet precipitate with hydrochloric acid and coloration with acetic acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 15296 of 1885; 2213 and 6687 of 1886; D. R. P. 39096; F. P. 160722, 163172; A. P. 344971, 358865.

Brilliant Congo G (A.) (By.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2. \end{array}$$

From tetrazotised benzidine, β-naphthylamine-3 : 6-disulphonic acid and β-naphthylamine-6-sulphonic acid (Brönner's). Aqueous solution gives a brownish-violet precipitate with hydrochloric acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 6687 of 1887; D. R. P. 41095; F. P. 160722.

Heliotrope 2 B (A.) (By.) (L.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH. \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-4 : 8-disulphonic acid and β-naphthol-8-sulphonic acid. Reddish-violet aqueous solution gives a bluish-violet precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. Solution in strong sulphuric acid is blue, becoming reddish-violet on dilution, and finally giving a violet precipitate.

Literature.—E. P. 1346 of 1888; D. R. P. 45342.

Trisulphone Violet B (K. S.); **Trisulphone Blue R** (K. S.); **Trisulphone Blue B** (K. S.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_3\cdot OH \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH. \end{array}$$

The first-named (for which the formula is given) is prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-3 : 6 : 8-trisulphonic acid and β-naphthol. The second and last colouring matters are prepared from tetrazotised tolidine and dianisidine respectively instead of benzidine. The solutions in water are violet to blue, and give bluish-violet to blue precipitates with hydrochloric acid. With sodium hydroxide the aqueous solutions become reddish-violet. The solutions in strong sulphuric acid are greenish-blue, giving violet precipitates on dilution.

Literature.—E. P. 4703 of 1897; F. P. 264279; A. P. 584981.

Chicago Blue 4 R (A.); **Benzo Blue 4 R** (By.); **Columbia Blue R** (A.); **Benzo Red Blue R** (By.). The first two and the last two respectively are probably identical. These colouring matters are produced from benzidine, and 1 mol. each of aminonaphthol-sulphonic acid (1 : 8 : 4) or -disulphonic acid (1 : 8 : 2 : 4) and a naphthol-sulphonic acid. Chicago blue 4 B gives a violet-blue and Columbia blue R a pure blue aqueous solution. Both solutions give a blue precipitate with hydrochloric acid. With sodium hydroxide the former becomes reddish-violet, and the latter blue. The solutions in strong sulphuric acid are cornflower blue, giving precipitates on dilution.

Diamine Violet N (C.); **Chlorazol Violet B** (H.); **Dianol Violet N** (Lev.); **Azidine Violet DV** (C. J.); **Naphthamine Violet N** (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2.C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared by the action of tetrazotised benzidine on 2 mols. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) in acid solution. The reddish-violet aqueous solution gives a violet-black precipitate with hydrochloric acid. The solution in strong sulphuric acid is greenish-blue, giving a reddish-violet precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 55648; F. P. 201770.

Diamine Black RO (C.); **Naphthamine Black BVE** (K.). Isomeric with the preceding. The combination is effected in alkaline solution whereby the azo- group enters the 2- position with respect to the hydroxy- group, whereas in the preceding case the azo- group enters the 8- position (ortho to the amino- group). The violet-black aqueous solution gives a blue precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a reddish-blue precipitate on dilution.

Literature.—As above.

Naphthamine Black RE (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 2 mols. of 1 : 8-aminonaphthol-6-sulphonic acid.

Literature.—D. R. P. appl. K 11223.

Benzo Violet R (By.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH.$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-4-sulphonic acid and α-naphthol-3 : 6-disulphonic acid. The reddish-violet aqueous solution gives a soluble violet precipitate with hydrochloric acid, and becomes red with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a violet precipitate on dilution.

Naphthylamine Diazo Black (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of 8-amino-α-naphthol-3 : 5-disulphonic acid (K- acid), and 7-amino-α-naphthol-3-sulphonic acid (γ-acid).

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563383.

Diamine Brown V (C.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_6H_3(NH_2)_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) and *m*-phenylenediamine. Brown-red aqueous solution gives a chocolate-brown precipitate with hydrochloric acid, and purplish-brown precipitate with sodium hydroxide. Solution in strong sulphuric acid is bluish-violet, giving a purplish-brown precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857; F. P. 201770.

Diamine Black BH (C.); **Dianol Blue BH** (Lev.); **Diazo Black BHN** (By.); **Renolamine Black BH** (T. M.); **Azidine Black BHN** (C. J.); **Ingrain Black 2 B** (H.); **Naphthamine Black CE** (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of 7-amino-α-naphthol-3-sulphonic acid and 8-amino-α-naphthol-3 : 6-disulphonic acid (H- acid). The reddish-blue aqueous solution becomes violet with hydrochloric acid and reddish-violet with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 1742 of 1891; D. R. P. 68462; F. P. 233032.

Oxamine Violet (B.); **Chlorazol Violet R** (H.); **Naphthamine Violet BE** (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared from tetrazotised benzidine and 6-amino-α-naphthol-3-sulphonic acid (2 mols.). The combination is effected in alkaline solution. The reddish-violet aqueous solution gives a violet precipitate with acids or alkalis. The solution in strong sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 2614 of 1893; D. R. P. 75469; F. P. 227892; A. P. 521096.

Diamine Blue BB (C.); **Benzo Blue BB** (By.) (Lev.); **Congo Blue 2 BX** (A.); **Direct Blue V** (P.); **Azidine Blue 2 B** (C. J.); **Chlorazol Blue RB** (H.); **Naphthamine Blue 2 BX** (K.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2.$$

Prepared by combining tetrazotised benzidine in alkaline solution with 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid; 2 mols.). The reddish-blue aqueous solution is unchanged by acids or alkalis. The solution in strong sulphuric acid is blue, becoming violet on dilution.

Literature.—E. P. 13443 of 1890; 1742 of 1891; D. R. P. 74593; F. P. 210033; A. P. 464135.

Naphthamine Blues 2B, 3B and 5B (K.). These are derived form tetrazotised benzidine, tolidine, etc., and 8-amino-α-naphthol-3 : 5-disulphonic acid (K-acid). The blue aqueous solution

gives a blue precipitate with hydrochloric acid and turns reddish-violet with sodium hydroxide. The solution in strong sulphuric acid is bluish-green.

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563385, 563386.

Direct Gray R (I.):

$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(OH)_2(CO_2H){\cdot}SO_3H$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(OH)_2(CO_2H){\cdot}SO_3H.$$

Prepared from tetrazotised benzidine and 1 : 7-dihydroxy-6-carboxynaphthalene-3-sulphonic acid (2 mols.). The violet aqueous solution gives a bluish-grey precipitate with hydrochloric acid and becomes dull violet-red with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a bluish-grey precipitate on dilution. The corresponding colour from tolidine is **Direct Gray B.**

Literature.—E. P. 14253 of 1892; D. R. P. 75258; F. P. 220468; A. P. 493564.

Dianol Red 2 B (Lev.); **Azidine Purpurine 10 B** (C. J.):

$$C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2$$
$$|$$
$$C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2.$$

Prepared from tetrazotised dichlorobenzidine (NH_2 : Cl = 4 : 3), and naphthionic acid (2 mols.). The red aqueous solution becomes violet with hydrochloric acid. The solution in strong sulphuric acid is blue, changing to violet on dilution.

Literature.—E. P. 25725 of 1896; F. P. 265135; A. P. 640743.

Dianol Brilliant Red (Lev.); **Toluylene Red** (O.); **Chlorantine Red 8 B** (I.); **Acetopurpurine** (A.); **Diphenyl Red 8 B** (G.); **Azidine Brilliant Red 8 B** (C. J.):

$$C_6H_2Cl{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2$$
$$|$$
$$C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2.$$

Prepared from tetrazotised dichlorobenzidine and β-naphthylamine-3 : 6-disulphonic acid. The bluish-red aqueous solution becomes slightly darker with hydrochloric acid. The solution in strong sulphuric acid is blue, becoming red on dilution.

Literature.—E. P. 25725 of 1896; D. R. P. 94410, 97101; F. P. 265135; A. P. 625174.

Anthracene Red (I.) (By.):

$$NO_2{\cdot}C_6H_3{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared by combining tetrazotised nitrobenzidine first with 1 mol. of salicylic acid and then with 1 mol. of α-naphthol-4-sulphonic acid. (The same colour is not produced by inverting the order of combination.) The red aqueous solution gives a red precipitate with hydrochloric acid. The solution in strong sulphuric acid is carmine-red, giving a brownish-red precipitate on dilution.

Literature.—E. P. 13475 of 1892; D. R. P. 72867; F. P. 223176; A. P. 493583.

Salicine Red G (K.). Prepared from tetrazotised nitrobenzidine and 1 mol. each of salicylic acid and β-naphthol, the product being sulphonated.

Literature.—E. P. 9454 of 1895; D. R. P. 87484.

Salicine Yellow G (K.). Prepared from tetrazotised nitrobenzidine and salicylic acid (2 mols.), the product being sulphonated. The orange aqueous solution is precipitated with hydrochloric acid and becomes reddish-brown with sodium hydroxide. The solution in strong sulphuric acid is orange-yellow, and gives a brown precipitate on dilution.

Literature.—As above, and Chem. Ind. 1896 19, 552.

Sulphone Azurine (By.) (A.) (L.) (Lev.):

$$SO_2\begin{cases}C_6H_2(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_5\\ |\\ C_6H_2(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_5.\end{cases}$$

Prepared from tetrazotised benzidinesulphone-disulphonic acid and phenyl-β-naphthylamine (2 mols.). The blue aqueous solution gives blue precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is violet, giving a blackish-violet precipitate on dilution.

Literature.—E. P. 1099 of 1884; D. R. P. 27954, 33088; A. P. 432989; Ber. 1889, 22, 2459.

Pyramine Orange R (B.):

$$SO_3H{\cdot}C_6H_3{\cdot}N_2{\cdot}C_6H_2(NH_2)_2{\cdot}NO_2$$
$$|$$
$$SO_3H{\cdot}C_6H_3{\cdot}N_2{\cdot}C_6H_2(NH_2)_2{\cdot}NO_2.$$

Prepared from tetrazotised benzidinedisulphonic acid and 6-nitro-*m*-phenylenediamine (2 mols.). The orange-red aqueous solution gives a yellowish-red precipitate with hydrochloric acid or sodium hydroxide. The solution in strong sulphuric acid is yellow, giving a yellowish-red precipitate on dilution.

Literature.—E. P. 8564 of 1894; D. R. P. 80973; F. P. 238340; A. P. 545333.

Carbazole Yellow (B.):

$$NH\begin{cases}C_6H_2{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH\\ |\\ C_6H_2{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH.\end{cases}$$

Prepared from tetrazotised diaminocarbazole and salicylic acid (2 mols.). The brownish-yellow aqueous solution gives a brown precipitate with hydrochloric acid, and becomes orange-yellow with sodium hydroxide. The solution in strong sulphuric acid is violet-blue, giving a brown precipitate on dilution.

Literature.—E. P. 14478 and 14479 of 1888; D. R. P. 46438; F. P. 193212; A. P. 401634.

Pyramidol Brown T (P. L.):

$$C_7H_6{\cdot}N_2{\cdot}C_6H_3(OH)_2$$
$$|$$
$$C_7H_6{\cdot}N_2{\cdot}C_6H_3(OH)_2.$$

Prepared from tetrazotised tolidine and resorcinol (2 mols.). The reddish-brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes brownish-red with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a blackish-brown precipitate on dilution. When the fibre is treated with diazo- solutions a deep brown is obtained.

Toluylene Orange G (O.) (By.) (A.); **Kanthosine J**; **Azidine Orange G** (C. J.):

$$C_7H_6{\cdot}N_2{\cdot}C_7H_5(CO_2H){\cdot}OH$$
$$|$$
$$C_7H_6{\cdot}N_2{\cdot}C_7H_4(NH_2)_2{\cdot}SO_3H.$$

Prepared from tetrazotised tolidine and 1 mol. each of hydroxytoluic acid (CH_3 : OH : CO_2H = 1 : 2 : 3) and *m*-tolylenediaminesulphonic acid

($CH_3 : NH_2 : NH_2 : SO_3H = 1 : 2 : 4 : 5$). The brownish-yellow aqueous solution gives a yellowish-brown precipitate with hydrochloric acid, and becomes reddish-orange with sodium hydroxide. The solution in strong sulphuric acid is magenta-red, giving a brown precipitate on dilution.

Literature.—E. P. 7997 of 1888; D. R. P. 47235; A. P. 396634.

Toluylene Orange R (O.); **Kanthosine R**; **Azidine Orange R** (C. J.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_7H_4(NH_2)_2{\cdot}SO_3H \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_7H_4(NH_2)_2{\cdot}SO_3H. \end{array}$$

Prepared from tetrazotised tolidine and *m* tolylenediaminesulphonic acid (2 mols.). The orange aqueous solution gives a bluish-red precipitate with hydrochloric acid. The solution in strong sulphuric acid is brown, giving a reddish precipitate on dilution.

Literature.—E. P. 4492 of 1887; D. R. P. 40905.

Benzopurpurine B (By.) (A.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2. \end{array}$$

Prepared by the action of diazotised tolidine on β-naphthylamine-6-sulphonic acid (2 mols.) in presence of alkali. Aqueous solution, orange-red; unchanged by sodium hydroxide; a brownish-red precipitate by dilute sulphuric acid. Dissolves in strong sulphuric acid with a blue colour, giving a brown precipitate on dilution.

References as for the next colouring matter.

Benzopurpurine 4 B (By.) (A.) (Lev.) (T. M.); **Cotton Red 4 B** (B.) (K.) (O.); **Cotton Red BP** (P.); **Sultan Red 4 B** (H.); **Diamine Red 4 B** (C.); **Dianil Red 4 B** (M.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2. \end{array}$$

Prepared by the action of diazotised tolidine on naphthionic acid (2 mols.). About twice the theoretical amount of naphthionic acid is used, the excess being regained from the filtrate after separating the colour. The alternative method of preparation by oxidising toluene-azonaphthionic acid (*cp.* Congo Red) is not used technically. Homologous with Congo Red, and isomeric with the last. Aqueous solution orange-red, giving a red precipitate with excess of sodium hydroxide; blue precipitate with hydrochloric acid; dissolves in strong sulphuric acid with a pure blue colour.

Literature.—E. P. 3803 of 1885, 6697 of 1895; D. R. P. 35615, 84893; F. P. 167876, 248210; A. P. 329632.

Benzopurpurine 6 B (Lev.) (By.) (A.). Prepared as above from tetrazoditolyl and Laurent's α-naphthylamine-5-sulphonic acid. Colouring matter very similar in properties to the preceding. References as above. The same constitution is assigned to **Diazo Brilliant Black B** (By.), which gives blues or blacks when diazotised and developed on the fibre.

Deltapurpurine 5 B (By.) (A.) (K.); **Diamine Red B** (A.) (By.) (L.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2. \end{array}$$

Prepared from tetrazoditolyl and 1 mol. of crude β-naphthylamine-δ-sulphonic acid and 1 mol. of the 6-sulphonic acid. Owing to the δ-acid being a mixture of isomerides (the 2 : 7- and 2 : 6-acids), the colouring matter contains also benzopurpurine B and deltapurpurine 7 B (*see* below). Aqueous solution orange, giving a brown coloration with acetic acid, and a brown precipitate with hydrochloric acid. Red precipitate with sodium hydroxide. Solution in strong sulphuric acid blue, giving a brown precipitate on dilution.

Literature.—E. P. 5846 of 1886; D. R. P. 42021; Ber. 1887, 20, 1430, 2910, 3160, 3353.

Diamine Red 3 B (C.); **Deltapurpurine 7 B** (By.) (A.). Isomeric with the preceding. Prepared from diazotised tolidine and β-naphthylamine-7-sulphonic acid. The colouring matter is precipitated from its aqueous solution by acetic acid, and forms an insoluble calcium salt. Red precipitate with sodium hydroxide. Solution in strong sulphuric acid blue, giving brown precipitate on dilution.

Literature.—E. P. 4846 and 12908 of 1886; D. R. P. 41201, 48074; Ber. 1887, 20, 2910, 3160.

Brilliant Purpurine R (A.) (By.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of β-naphthylamine-3 : 6-disulphonic acid and naphthionic acid. The red aqueous solution gives a black precipitate with hydrochloric acid, and a red one with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a blue-black precipitate on dilution.

Literature.—E. P. 6687 of 1887; D. R. P. 41095; F. P. 160722.

Azo- Blue (By.) (A.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH. \end{array}$$

Prepared by the action of diazotised tolidine on α-naphthol-4-sulphonic acid. Aqueous solution of colouring matter violet, becoming crimson on addition of sodium hydroxide; restored to violet by dilute sulphuric acid. Dissolves in strong sulphuric acid with a pure blue colour, giving violet precipitate on dilution.

Literature.—E. P. 9510 of 1885; D. R. P. 35341; F. P. 171133; A. P. 366078.

Congo Corinth B (By.) (A.); **Dianil Bordeaux B** (M.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH. \end{array}$$

From diazotised tolidine, naphthionic acid, and α-naphthol-4-sulphonic acid. Aqueous solution magenta-red, giving violet precipitate with mineral acids. Blue solution in strong sulphuric acid; violet precipitate on dilution.

Literature.—E. P. 15296 of 1885; 2213 and 6687 of 1886; D. R. P. 39096; A. P. 358865.

Congo Red 4 R

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_6H_3(OH)_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2. \end{array}$$

From diazotised tolidine, resorcinol, and naphthionic acid. Aqueous solution brownish-red, violet precipitate with mineral acids, brown

precipitate with acetic acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 15296 of 1885; 2213 of 1886; D. R P. 39096.

Brilliant Congo R (A.) (By.); **Azidine Scarlet B** (C. J.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2. \end{array}$$

From diazotised tolidine, β-naphthylamine-3 : 6-disulphonic acid and β-naphthylamine-6-sulphonic acid (Brönner's). Aqueous solution brownish-red, giving a similarly coloured precipitate with mineral acids. Solution becomes bluer with acetic acid. Orange precipitate with sodium hydroxide. Blue solution in strong sulphuric acid, giving dark-brown precipitate on dilution.

Literature.—E. P. 6687 of 1887; D. R. P. 41095.

Azo- Black Blue (O.); **Azo- Navy Blue** (O.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_6H_3(OH)(NH_2)\cdot NH\cdot C_6H_5 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of *m*-hydroxydiphenylamine and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). Solution in water is brownish-violet and in strong sulphuric acid blue, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 10861 of 1891; D. R. P. 70201; A. P. 402415.

Azo- Mauve (O.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_6\cdot NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) and α-naphthylamine. Violet aqueous solution gives a violet precipitate with hydrochloric acid, and becomes rather bluer with dilute acetic acid. Solution in strong sulphuric acid is blue, becoming violet on dilution.

Literature.—As above.

Azidine Wool Blue R (C. J.).—

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of δ-naphthol-8-sulphonic acid and 8-amino-α-naphthol-5-sulphonic acid. The corresponding colour from dianisidine is **Azidine Wool Blue B** (C. J.).

Literature.—E. P. 27609 of 1907; D. R. P. 203535, 209269; F. P. 383747; A. P. 888036.

Oxamine Blue 3 R (B.); **Azidine Blue 3 RN** (C. J.); **Naphthamine Blue 3 RE** (K.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of 6-amino-α-naphthol-3-sulphonic acid and α-naphthol-4-sulphonic acid. Violet aqueous solution is precipitated with hydrochloric acid or sodium hydroxide. Solution in strong sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 2614 of 1893; D. R. P. 93276; F. P. 227892; A. P. 521095.

Columbia Blue G (A.); **Chicago Blue 2 R** (A.). These colouring matters are produced from tetrazotised tolidine and 1 mol. each of 8-amino-α-naphthol-5-sulphonic acid (S-acid) and a naphtholsulphonic acid. Columbia blue G gives a blue solution, which is precipitated with hydrochloric acid, and turned reddish-violet with sodium hydroxide. Its solution in strong sulphuric acid is greenish-blue, giving a reddish-violet precipitate on dilution. Chicago blue 2 R forms a violet-blue solution, becoming pure blue with hydrochloric acid, and reddish-violet with sodium hydroxide. Its solution in strong sulphuric acid is cornflower blue, giving a blue precipitate on dilution.

Chicago Blue R (A.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 8-amino-α-naphthol-5-sulphonic acid (2 mols.). The violet-blue solution gives a dark-violet precipitate with hydrochloric acid. The solution in strong sulphuric acid is cornflower blue, giving a bluish-violet precipitate on dilution. The corresponding colour from dianisidine is **Chicago Blue B** (A.).

Literature.—A. P. 506284.

Dianil Blue B (M.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2. \end{array}$$

Prepared from tetrazotised tolidine and 2 mols. of 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotrope acid). The blue aqueous solution is not changed with hydrochloric acid or sodium hydroxide. The solution in strong sulphuric acid is deep-blue, becoming bluish-violet on dilution.

The corresponding colour from benzidine is **Dianil Blue R**, and from dianisidine **Dianil Blue G**.

Diamine Blue 3 B (C.); **Benzo Blue 3 B** (By.); **Congo Blue 3 B** (A.) (Lev.); **Azidine Blue 3 B** (C. J.); **Chlorazol Blue 3 B** (H.); **Naphthamine Blue 3 BX** (K.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2. \end{array}$$

Prepared from tetrazotised tolidine and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid; 2 mols.). The violet aqueous solution becomes bluer with hydrochloric acid, and gives a precipitate with excess. The solution in strong sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 13443 of 1890; 1742 of 1891; D. R. P. 74593; F. P. 210033.

Diamine Blue BX (C.); **Benzo Blue BX** (By.); **Congo Blue BX** (A.) (Lev.); **Azidine Blue BX** (C. J.); **Naphthamine Blue BXR** (K.):

$$\begin{array}{l} C_7H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2 \\ | \\ C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH. \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of α-naphthol-4-sulphonic acid and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). The bluish-violet aqueous solution gives a violet precipitate with hydrochloric acid, and becomes bluish-red with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 1742 of 1891; D. R. P. 74593.

Direct Blue R (I.):

$$C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(OH)_2{\cdot}SO_3H$$
$$|$$
$$C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared from tetrazotised tolidine and 1 mol. each of 1 : 7-dihydroxy-6-carboxynaphthalene-3-sulphonic acid and α-naphthol-4-sulphonic acid. The violet aqueous solution gives a violet precipitation with hydrochloric acid, and becomes violet-red with sodium hydroxide. The solution in strong sulphuric acid is blue. The corresponding colour from dianisidine is **Direct Blue B** (I.).

Literature.—E. P. 14253 of 1892; D. R. P. 75258; F. P. 220468; A. P. 493563, 493564.

Indazurine BM (Bl.). Isomeric with the preceding. A different naphthoic acid, viz.: 1 : 7-dihydroxy-2-carboxynaphthalene-4-sulphonic acid is used, the other constituents being the same. The violet-blue aqueous solution becomes bluer with hydrochloric acid and red with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a violet precipitate on dilution. The corresponding colour from dianisidine is **Indazurine G. M.** (Bl.).

Literature.—A. P. 524070.

Indazurine TS (Bl.):

$$C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(OH)_2{\cdot}SO_3H$$
$$|$$
$$C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared as the preceding, except that 7-amino-α-naphthol-3-sulphonic acid is used instead of α-naphthol-4-sulphonic acid. The violet-blue aqueous solution becomes redder with acids or alkalis. The solution in strong sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—As above.

Diamine Yellow N (C.):

$$C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_5.$$

Prepared by combining tetrazotised ethoxybenzidine first with salicylic acid (1 mol.) and then with phenol (1 mol.) and ethylating the product. The yellow aqueous solution gives a greenish precipitate with hydrochloric acid and a reddish-yellow with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a greenish-brown precipitate on dilution.

Literature.—E. P. 14464 of 1887; D. R. P. 46134; F. P. 186566, 186567; A. P. 380067.

Diamine Blue 3 R (C.):

$$C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared from tetrazotised ethoxybenzidine and α-naphthol-4-sulphonic acid (2 mols.). The reddish-blue aqueous solution is not changed with hydrochloric acid, but becomes reddish-violet with sodium hydroxide. The solution in strong sulphuric acid is dark blue, giving a violet precipitate on dilution.

Literature.—As above.

Diamine Blue B (C.):

$$C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared from tetrazotised ethoxybenzidine and 1 mol. each of β-naphthol-3 : 7-disulphonic acid and α-naphthol-4-sulphonic acid. The blue aqueous solution gives a blue precipitate with hydrochloric acid, and becomes reddish-blue with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—As above.

Diamine Blue Black E (C.):

$$C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$
$$|$$
$$C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared as the preceding, except that 7-amino-α-naphthol-3-sulphonic acid is used instead of α-naphthol-4-sulphonic acid. The combination is effected in alkaline solution. The blackish-blue aqueous solution gives a blue precipitate with hydrochloric acid, and is not changed with sodium hydroxide. The solution in strong sulphuric acid is blackish-blue, giving a blue precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857.

Diazurine B (By.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2$$
$$|$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2.$$

Prepared from tetrazotised dianisidine and α-naphthylamine-5-sulphonic acid (Laurent's acid) (2 mols.). The brownish-red aqueous solution gives a blue precipitate with hydrochloric acid and a soluble red one with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.

Benzopurpurine 10 B (By.) (Lev.) (K.); **Sultan 10 B** (H.). Isomeric with the preceding. Prepared from tetrazotised dianisidine and 2 mols. of naphthionic acid. The carmine-red aqueous solution gives a blue precipitate with hydrochloric acid and a red one with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 14424 of 1885; D. R. P. 38802; F. P. 173042; A. P. 481954.

Azo- Violet (By.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2$$
$$|$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Tetrazotised dianisidine (1 mol.) is combined with 1 mol. of naphthionic acid, and then with 1 mol. of α-naphthol-4-sulphonic acid. Aqueous solution reddish-violet, giving blue precipitate with mineral acids and bluish-violet coloration with acetic acid. Solution turned magenta by sodium hydroxide. Dissolves with a blue colour in strong sulphuric acid, giving a blue precipitate on dilution.

Literature.—E. P. 14424 of 1885; 7283 of 1886; D. R. P. 40247; F. P. 173042; A. P. 447302.

Benzoazurine G (By.) (A.) (L.) (Lev.) (K.); **Bengal Blue G** (O.); **Oxamine Blue A** (B.); **Azidine Blue BA** (C. J.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$
$$|$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.$$

Prepared by the action of tetrazotised dianisidine on α-naphthol-4-sulphonic acid. Aqueous solution bluish-violet, becoming red on addition of sodium hydroxide; dark-violet precipitate

with dilute hydrochloric acid. Dissolves in strong sulphuric acid with a blue colour, giving violet precipitate on dilution. **Benzoazurine R** is a mixture of benzoazurine G and azo blue.

Literature.—E. P. 14424 of 1885; D. R. P. 38802; F. P. 173042; A. P. 357273.

Benzoazurine 3 G (By.) (A.) (L.) (Lev.) (K.). Isomeric with the above. α-Naphthol-5-sulphonic acid (Laurent's acid) is used instead of the 4-sulphonic acid. Aqueous solution bluish-violet, giving bluish-violet precipitate with hydrochloric acid and becoming violet-red with sodium hydroxide. Solution in strong sulphuric acid is blue, giving violet precipitate on dilution.

Literature.—As above.

Chlorazol Blue R and **3 G** (H.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4Cl(SO_3H){\cdot}OH$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4Cl(SO_3H){\cdot}OH.$$

Prepared from tetrazotised dianisidine and 2 mols. of chloro-α-naphthol-4- or 5-sulphonic acid. The violet aqueous solution undergoes little change with hydrochloric acid, but turns crimson with sodium hydroxide. The solution in strong sulphuric acid is greenish-blue (R) or green (3 G).

Literature.—E. P. 12085 of 1898.

Diamine Brilliant Blue G (C.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3Cl(SO_3H)_2{\cdot}OH$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3Cl(SO_3H)_2{\cdot}OH.$$

Prepared from tetrazotised dianisidine and 2 mols. of 8-chloro-α-naphthol-3 : 6-disulphonic acid. Bluish-violet aqueous solution gives a soluble violet precipitate with hydrochloric acid, and becomes cherry-red with sodium hydroxide. Solution in strong sulphuric acid is greenish-blue, turning violet on dilution.

Literature.—E. P. 1920 of 1894; D. R. P. 79055, 82285; F. P. 235271; A. P. 532125, 535037.

Oxamine Blue B (B.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2.$$

Prepared from tetrazotised dianisidine and 1 mol. each of 5-amino-α-naphthol-3-sulphonic acid and α-naphthol-4-sulphonic acid. Dark-blue aqueous solution turns reddish-violet with sodium hydroxide, and pale violet with hydrochloric acid. The solution in strong sulphuric acid is bluish-green, becoming violet on dilution.

Literature.—E. P. 2370 of 1893; D. R. P. 82572; F. P. 229263; A. P. 558344.

Chicago Blue 6 B [1] (A.); **Benzo Brilliant Blue 6 B** (By.); **Diamine Sky Blue FF** (C.); **Azidine Sky Blue FF** (C. J.); **Chlorazol Sky Blue FF** (H.); **Dianol Brilliant Blue 6 B** (Lev.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2.$$

Prepared from tetrazotised dianisidine and 2 mols. of 8-amino-α-naphthol-5 : 7-disulphonic acid (S-acid). The combination is effected in alkaline solution. Blue aqueous solution is not changed with hydrochloric acid, but becomes bluish-violet with sodium hydroxide. Solution in strong sulphuric acid is bluish-green, becoming pure blue on dilution.

Diamine Sky Blue (C.); **Benzo Sky Blue** (By.); **Congo Sky Blue** (A.); **Dianol Sky Blue** (Lev.); **Renol Pure Blue** (T. M.); **Azidine Sky Blue** (C. J.); **Chlorazol Blue 6 G** (H.); **Naphthamine Blue 7 B** (K.). Isomeric with the preceding. Two mols. of 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) are used as components. Blue aqueous solution is not changed with hydrochloric acid, but becomes redder with sodium hydroxide. Solution in strong sulphuric acid is bluish-green, becoming pure blue on dilution.

Literature.—E. P. 1742 of 1891; D. R. P. 74593; F. P. 201770; A. P. 464135.

Indazurine B (Bl.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2.$$

Prepared from tetrazotised dianisidine and 1 mol. each of 1 : 7-dihydroxynaphthalene-4-sulphonic acid and β-naphthol-3 : 6-disulphonic acid. Blue aqueous solution turns bluer with hydrochloric acid and red with sodium hydroxide. Solution in strong sulphuric acid is blue, giving a reddish-blue precipitate on dilution.

Literature.—D. R. P. 524069.

Brilliant Azurine 5 G (By.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2.$$

Prepared by combining tetrazotised dianisidine with 2 mols. of 1 : 8-dihydroxynaphthalene-4-sulphonic acid in acetic acid solution. Aqueous solution is bluish-violet; with hydrochloric acid gives a blue precipitate, and with sodium hydroxide becomes red. Solution in strong sulphuric acid is greenish-blue, giving a dark reddish-blue precipitate on dilution.

Literature.—E. P. 13665 of 1889; D. R. P. 57166; F. P. 173042; A. P. 417294.

Indazurine BB (Bl.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(SO_3H)(OH)_2$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH.$$

Prepared from tetrazotised dianisidine and 1 mol. each of 1 : 7-dihydroxy-2-carboxynaphthalene-4-sulphonic acid and β-naphthol-3 : 6-disulphonic acid (R-salt). Blue aqueous solution becomes slightly bluer with hydrochloric acid, and redder with sodium hydroxide. Solution in strong sulphuric acid is greenish-blue, giving a blue precipitate on dilution.

Literature.—A. P. 524070.

Indazurine 5 GM (Bl.):

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(SO_3H)(OH)_2$$
$$\vert$$
$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2.$$

Prepared as the preceding, except that 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) is used instead of R-salt. The pure blue aqueous solution is not changed with hydrochloric acid, but becomes redder with sodium hydroxide. The solution in strong sulphuric acid is bluish-green, becoming bluish-violet on dilution.

Literature.—As above.

Hessian Yellow (L.) (A.) (By.):

$$CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$
$$\Vert$$
$$CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH.$$

[1] **Chicago Blue 4 B** and **RW** and **Dianol Blue RW** (Lev.) are mixed azo-dyestuffs from dianisidine, S-acid, and another component.

Prepared from tetrazotised diaminostilbenedisulphonic acid [1] and salicylic acid. Aqueous solution ochreous, giving blackish precipitate with mineral acids. Solution reddened by sodium hydroxide. Reddish-violet solution in strong sulphuric acid, giving blackish precipitate on dilution.

Literature.—E. P. 4387 of 1886; D. R. P. 38735; A. P. 350229, 350230.

Hessian Purple N (L.) (A.) (By.):

$$\begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot NH_2 \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot NH_2. \end{matrix}$$

From tetrazotised diaminostilbenedisulphonic acid and β-naphthylamine. Aqueous solution red, giving bluish-black precipitate with mineral acids, and violet-black precipitate with acetic acid. Red coloration or precipitate with sodium hydroxide. Blue solution in strong sulphuric acid, giving bluish-black precipitate on dilution.

References as in preceding.

Hessian Purple B (L.) (A.) (By.):

$$\begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2. \end{matrix}$$

Prepared by the action of tetrazostilbenedisulphonic acid (1 mol.) on 2 mols. of crude β-naphthylamine-3-sulphonic acid (a mixture of the 2 : 6- and 2 : 7- acids). Aqueous solution red, giving brownish-black precipitate with mineral acids. Reddish-violet precipitate with sodium hydroxide. Violet solution in strong sulphuric acid giving brown precipitate on dilution.

References as in preceding, and D. R. P. 40575.

Hessian Purple D. Isomeric with the preceding. Prepared from the above tetrazo-disulphonic acid and Dahl's β-naphthylamine-5-sulphonic acid. Aqueous solution orange, giving brown precipitate with mineral acids, and becoming redder with sodium hydroxide. Violet solution in strong sulphuric acid becoming brown on dilution.

References as in preceding.

Brilliant Yellow (L.) (A.) (By.):

$$\begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_4\cdot OH \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_4\cdot OH. \end{matrix}$$

From the same tetrazo-disulphonic acid and phenol. Aqueous solution orange, giving violet precipitate with mineral acids. Dissolves with a reddish-violet in strong sulphuric acid, giving a violet precipitate on dilution.

References as in preceding.

Chrysophenine (L.) (A.) (By.); **Chrysobarine G extra conc.** (T. M.); **Phenine Yellow** (P.); **Azidine Yellow CP** (C. J.):

$$\begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_4\cdot OH \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_4\cdot O\cdot C_2H_5. \end{matrix}$$

Prepared by ethylating the preceding colouring matter. Aqueous solution orange, giving brown precipitate with mineral acids. Dissolves with a reddish-violet colour in strong sulphuric acid, giving blue precipitate on dilution.

Literature.—E. P. 3994 of 1887; D. R. P. 42466; Ber. 1894, 27, 3357.

Hessian Violet (L.) (A.) (By.):

$$\begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot NH_2 \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH. \end{matrix}$$

Prepared by combining 1 mol. of tetrazotised diaminostilbenedisulphonic acid with 1 mol. of α-naphthylamine, and then with 1 mol. of β-naphthol. Aqueous solution reddish-violet, becoming bluer with acetic acid, and giving a blue precipitate with mineral acids. Solution in strong sulphuric acid blue, giving a violet precipitate on dilution.

Literature.—E. P. 4387 of 1886; D. R. P. 38735, 40575.

Brilliant Hessian Purple (L.) (A.) (By.):

$$\begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2. \end{matrix}$$

Prepared from tetrazotised diaminostilbenedisulphonic acid, and 2 mols. of β-naphthylamine-6-sulphonic acid. Purple-red aqueous solution gives bluish-black precipitate with hydrochloric acid and carmine-red precipitate with sodium hydroxide. Solution in strong sulphuric acid blue, giving a bluish-black precipitate on dilution.

References as for Hessian Yellow.

Stilbene Colouring Matters.

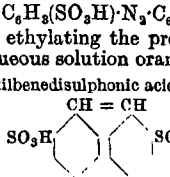
The colouring matters which have hitherto been classified under this head are produced by alkaline condensation and oxidation of *p*-nitrotoluenesulphonic acid under various conditions. They have generally been considered to be nitroso- or azoxy- stilbene derivatives, but the recent researches of A. G. Green and his collaborators have shown that all the colouring matters of this group must be regarded as azo-dyes (Chem. Soc. Trans. 1904, 85, 1424, 1432; J. Soc. Dyers, 1907, 23, 162). The first action of alkali hydroxide on *p*-nitrotoluenesulphonic acid leads to the formation of a dinitrosostilbenedisulphonic acid, one molecule of which is oxidised at the expense of a second molecule, and the remaining two nitrogen atoms of two molecules combine to form an azo- group in a distilbene molecule:

$$2\ \begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot NO \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot NO \end{matrix} \rightarrow \begin{matrix} CH\cdot C_6H_3(SO_3H)\cdot N{=}{=}N\cdot C_6H_3(SO_3H)\cdot CH \\ \| \qquad\qquad\qquad\qquad\qquad\qquad \| \\ CH\cdot C_6H_3(SO_3H)\cdot NO_2 \qquad NO_2\cdot C_6H_3(SO_3H)\cdot CH. \end{matrix}$$

The equation represents the formation of the greenest yellow of the series (stilbene yellow 8G: see below). The redder yellows and oranges may be regarded as formed therefrom by the reduction of the two nitro- groups, first to an azoxy- and finally to an azo- group.

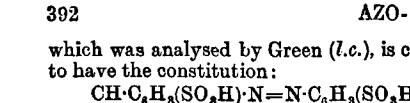
Sun Yellow (G.); **Afghan Yellow** (H.); **Curcumine S** (L.); **Naphthamine Yellow** (K.); **Direct Yellow J** (P.); **Azidine Fast Yellow G** (C. J.); **Direct Yellow RT** (Cl. Co.). Prepared by heating *p*-nitrotoluenesulphonic acid with aqueous sodium hydroxide. Direct yellow RT,

[1] Diaminostilbenedisulphonic acid



is prepared by boiling *p*-nitrotoluene-*o*-sulphonic acid with sodium hydroxide and reducing the product with zinc-dust.

which was analysed by Green (*l.c.*), is considered to have the constitution:



(the colouring matter being, of course, the sodium salt).

Aqueous solution is brownish-yellow. Solution in strong sulphuric acid is violet, becoming yellow on dilution.

Literature.—E. P. 4387 of 1886; D. R. P. 38735; F. P. 175630; A. P. 360553; Bull. Mulhouse, 1887, 99, Ber. 1886, 19, 3234.

Naphthamine Yellow G (K.); **Direct Yellow R** (By.); **Renol Yellow R** (T. M.). Prepared as above, but the temperature of the reaction is 60°-85°. Reddish-yellow aqueous solution gives brown precipitate with excess of hydrochloric acid and a yellow precipitate with sodium hydroxide. Solution in strong sulphuric acid is cherry-red, becoming yellow on dilution.

Literature.—E. P. 23672 of 1892; D. R. P. 79241; F. P. 226635; Ber. 1893, 26, 2233; 1895, 28, 2281.

Mikado Yellow (L.); **Milkado Gold Yellow 2 G, 4 G, 6 G, 8 G** (L.); **Naphthamine Yellow 2 G, 3 G** (L.). Prepared by treating the products of condensation of *p*-nitrotoluenesulphonic acid and sodium hydroxide with oxidising agents. Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid, and yellow solution or precipitate with sodium hydroxide. Solution in strong sulphuric acid is orange to red, becoming yellow on dilution.

Literature.—E. P. 23672 of 1892; D. R. P. 42466; F. P. 226635; Ber. 1893, 26, 2234; 1897, 30, 2618, 3097; 1898, 31, 354, 1078.

Stilbene Yellow G, 4 G, 6 G, 8 G (Cl. Co.). The constitution of the last brand has already been given. The colouring matters are alkaline condensation products of dinitrodibenzyldisulphonic acid, and dinitrostilbenedisulphonic acid. Solution in strong sulphuric acid is orange to yellowish-red, becoming yellow on dilution.

Literature.—E. P. 5351, 21553, 21399, of 1897; 3393 of 1898; D. R. P. 113513, 113514; F. P. 272384, 273018, 273037; Ber. 1897, 30, 3097; 1898, 31, 1078.

Diphenylcitronine G (G.). Prepared by condensing dinitrodibenzyldisulphonic acid with aniline in presence of sodium hydroxide or by condensing similarly dinitrostilbenedisulphonic acid. Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid, and an orange-yellow one with sodium hydroxide. Solution in strong sulphuric acid is orange, giving a brownish-yellow precipitate on dilution.

Literature.—E. P. 18990, 21399, 21553 of 1897; D. R. P. 101760, 113514; F. P. 269466, 273018; A. P. 613911.

Diphenyl Fast Yellow (G.). Prepared by condensing dinitrodibenzyldisulphonic acid or dinitrostilbenedisulphonic acid with primuline or dehydrothio-*p*-toluidinesulphonic acid in presence of sodium hydroxide. Yellow aqueous solution gives a brownish-orange yellow precipitate with hydrochloric acid, and an orange-yellow one with sodium hydroxide. Solution in strong sulphuric acid is red, giving a brownish-yellow precipitate on dilution.

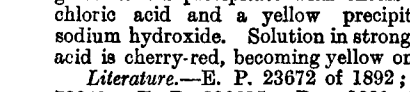
Literature.—E. P. 18990, 21399, 21553 of 1897; D. R. P. 100613, 113514; F. P. 269466, 273018.

Mikado Brown B, 3 GO, M (L.). Prepared by the action of alkalis on *p*-nitrotoluenesulphonic acid in presence of oxidisable substances. Brown aqueous solution gives a brown precipitate with hydrochloric acid. Solution in strong sulphuric acid is violet-black, giving a brown precipitate on dilution.

Literature.—E. P. 2664 of 1888; D. R. P. 46252, 48528; A. P. 395115, 396527.

Mikado Orange G to 4 R (L.); **Naphthamine Orange 2 R** (K.); **Direct Orange G** (G.). Prepared by the same reaction as the preceding, and by the action of alkaline reducing agents on direct yellow. Orange-yellow aqueous solution gives a dark-brown precipitate with hydrochloric acid, and an orange one with sodium hydroxide. Solution in strong sulphuric acid is violet to blue, giving a brown precipitate on dilution.

Mikado Orange 3 RO (L.) has the constitution:



Brands **4 RO** and **5 RO** are redder shades.

Literature.—E. P. 2664 of 1888; D. R. P. 46252, 48528, 46929; F. P. 189697; A. P. 395115, 396527; Ber. 1893, 26, 2233; 1895, 28, 2281.

Polychromine R (G.); **Fast Cotton Brown R** (G.); **Direct Brown R** (G.). Prepared by boiling equal molecules of *p*-nitrotoluenesulphonic acid and *p*-phenylenediamine with sodium hydroxide. Orange-brown aqueous solution gives a blue-black precipitate with hydrochloric acid. Solution in strong sulphuric acid is reddish-violet, giving a bluish-black precipitate on dilution.

Literature.—E. P. 15671 of 1890; D. R. P. 59290; F. P. 208626; A. P. 455952.

Diphenyl Orange RR (G.); **Azidine Orange D 2 R** (C. J.). Prepared by condensing 2 mols. of *p*-nitrotoluenesulphonic acid with 2 mols. of *p*-phenylenediamine in presence of concentrated aqueous sodium hydroxide. Orange-yellow aqueous solution gives a bluish-black precipitate with hydrochloric acid, and an orange one with sodium hydroxide. Solution in strong sulphuric acid is red, giving a bluish-black precipitate on dilution.

Literature.—E. P. 6651 of 1899; D. R. P. appl. G 13069; F. P. 286620; A. P. 636065.

Chicago Orange RR (G.). Prepared by condensing *p*-nitrotoluenesulphonic acid with benzidine in presence of sodium hydroxide. Orange-yellow aqueous solution gives a brown precipitate with hydrochloric acid, and an orange-brown one with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a brown precipitate on dilution.

Literature.—E. P. 788 of 1893; D. R. P. 75326; F. P. 227271.

Arnica Yellow (G.). Prepared by condensing *p*-nitrotoluenesulphonic acid with *p*-aminophenol in presence of boiling aqueous sodium hydroxide. Brownish-yellow aqueous solution gives a brownish-black precipitate with hydrochloric acid. Solution in strong sulphuric acid is violet, giving a dark-brown precipitate on dilution.

Literature.—F. P. 222554.

Diphenyl Chrysoïne G (G.). Prepared by ethylating the preceding. Golden-yellow aqueous solution gives a blackish-brown precipitate with hydrochloric acid, and an orange one with sodium hydroxide. Solution in strong sulphuric acid is violet-red, giving a blackish-brown precipitate on dilution.

Literature.—E. P. 6651 of 1899; D. R. P. (appl. G.) 13069; F. P. 286620; A. P. 636065.

Diphenyl Chrysoïne RR (G.). Prepared by diazotising the condensation product of dinitrodibenzyldisulphonic acid and aniline in alkaline solution, combining the diazo- compound with phenol and ethylating the product. Reddish-orange aqueous solution gives a blackish-brown precipitate with hydrochloric acid, and a reddish-brown one with sodium hydroxide. Solution in strong sulphuric acid is pure blue, giving a brownish-black precipitate on dilution.

Literature.—E. P. 6651 of 1899; D. R. P. 117729; F. P. 286620; A. P. 644462.

Diphenyl Fast Brown G (G.). Prepared as the preceding, but the diazo- compound is combined with 7-phenylamine-α-naphthol-3-sulphonic acid. The dark yellowish-brown aqueous solution gives a blackish-brown precipitate with hydrochloric acid, and a dark-brown one with sodium hydroxide. Solution in strong sulphuric acid is dark blue, giving a blackish-brown precipitate on dilution.

References as above.

Diphenyl Catechine G (G.). Prepared as above, but the diazo- compound is combined with 7-dimethylamino-α-naphthol-3-sulphonic acid. Yellowish-brown aqueous solution gives a dark-brown precipitate with hydrochloric acid, and a brown one with sodium hydroxide. Solution in strong sulphuric acid is blackish violet blue, giving a blackish-brown precipitate on dilution.

References as above.

Curcuphenine (Cl. Co.). Prepared by condensing *p*-nitrotoluenesulphonic acid with dehydrothio-*p*-toluidinesulphonic acid in presence of very dilute aqueous sodium hydroxide. Yellow aqueous solution gives a brown precipitate with hydrochloric acid. The solution in strong sulphuric acid is red, giving a brownish-yellow precipitate on dilution.

Literature.—E. P. 12922 of 1896; D. R. P. 99575; F. P. 264755.

Chlorophenine Orange RR and RO (Cl. Co.) are reduction products of the preceding.

IV. Trisazo- Colouring Matters.[1]

These colours, as their name implies, contain three azo- groups.

Janus Brown B (M.):

$N(CH_3)_3Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_2(NH_2)_2{\cdot}N_2{\cdot}C_6H_5$.

Prepared by combining diazotised *m*-aminophenyltrimethylammonium chloride with α-naphthylamine, diazotising the product and combining with chrysoïdine. Aqueous solution is brown, giving a soluble brown precipitate with hydrochloric acid or sodium hydroxide. Solution in strong sulphuric acid is dark green, becoming brown on dilution.

Literature.—E. P. 9343 of 1896; D. R. P. 95530.

[1] Chrome patent green A (K.), which belongs to this series, is no longer in commerce.

Janus Brown R (M.) is prepared from diazotised *p*-aminobenzyldiethylamine and α-naphthylamine, the product being diazotised and combined with chrysoïdine, resorcinol, or *m*-phenylenediamine. Reactions are similar to those given by the preceding colour.

Literature.—E. P. 19976 of 1896; D. R. P. 99127; F. P. 256156; A. P. 610345.

Melogene Blue BH (K. S.); **Diamine Beta Black** (C.):

$$N_2\begin{cases}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2\\ C_{12}H_8{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2.\end{cases}$$

Tetrazotised benzidine is combined with 1 mol. of *p*-xylidine, the product diazotised and combined with 2 mols. of 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). The violet-blue aqueous solution gives a violet precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 28810 of 1896; F. P. 262109; A. P. 591616.

Direct Black V and **RR** (P.) are analogous colours derived from benzidine, 8-amino-α-naphtholsulphonic acid, a primary amine, and a *m*-diamine.

Benzo Gray (By.):

$$N_2\begin{cases}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH\\ C_{12}H_8{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH.\end{cases}$$

The colouring matter from tetrazotised benzidine and 1 mol. each of salicylic acid and α-naphthylamine is diazotised and combined with α-naphthol-4-sulphonic acid. The Bordeaux-brown aqueous solution gives a black precipitate with hydrochloric acid. The solution in strong sulphuric acid is blue, giving a black precipitate on dilution.

Literature.—E. P. 13235 of 1890; D. R. P. 57331; F. P. 187365.

Benzo Olive (By.):

$$N_2\begin{cases}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2\\ C_{12}H_8{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH.\end{cases}$$

Prepared as the preceding, except that 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) is used as the end component. The dark moss-green aqueous solution gives a blackish-grey precipitate with hydrochloric acid, and becomes dark brown with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a greenish-black precipitate on dilution.

Literature.—E. P. 3439 of 1891; D. R. P. 65480; F. P. 187365.

Congo Fast Blue R (A.):

$$N_2\begin{cases}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH\\ C_{14}H_{12}{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH.\end{cases}$$

Tolidine is tetrazotised and combined with 1 mol. of α-naphthylamine, the product diazotised and combined with 2 mols. of α-naphthol-3 : 8-disulphonic acid (ε-acid). The blue aqueous solution is precipitated with acids or alkalis. The solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 6932 of 1890; D. R. P. 60921.

Benzo Black Blue R (By.):

$$N_2\begin{cases}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH\\ C_{14}H_{12}{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH.\end{cases}$$

Tolidine is tetrazotised and combined with

1 mol. of α-naphthylamine and the intermediate product diazotised and combined with 2 mols. of α-naphthol-4-sulphonic acid. Bluish-violet aqueous solution gives a violet precipitate with hydrochloric acid. Solution in strong sulphuric acid is blue, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 16484 of 1887; F. P. 187365; A. P. 440639.

Benzo Indigo Blue (By.):

$$N_2\begin{cases}C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)_2\\ C_{14}H_{12}\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)_2.\end{cases}$$

The same intermediate tetrazo- compound as above is combined with 2 mols. of 1:8-dihydroxynaphthalene-4-sulphonic acid (S-acid). The violet aqueous solution gives a bluish-violet precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in strong sulphuric acid is greenish-blue, giving a violet-blue precipitate on dilution.

Literature.—E. P. 3397 of 1890; D. R. P. 57912; F. P. 200520: A. P. 501118.

Congo Fast Blue B (A.):

$$N_2\begin{cases}C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH\\ C_{14}H_{12}O_2\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.\end{cases}$$

Dianisidine is tetrazotised and combined with 1 mol. of α-naphthylamine and the intermediate product diazotised and combined with 2 mols. of α-naphthol-3:8-disulphonic acid (ε-acid). Blue aqueous solution gives a blue precipitate with acids or alkalis. Solution in strong sulphuric acid is cornflower blue, giving a blue precipitate on dilution.

Literature.—E. P. 6932 of 1890; D. R. P. 57444.

Columbia Black FB and **FF extra** (A.); **Azidine Black FF** (C. J.); **Titan Blacks** (H.):

$$N_2\begin{cases}C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2\\ C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_6H_3(NH_2)_2.\end{cases}$$

p-Aminoacetanilide is diazotised and combined with 7-amino-α-naphthol-3-sulphonic acid (γ-acid), the product saponified with sodium hydroxide, the resulting diamino-compound tetrazotised and combined first with 1 mol. of α-naphthylamine-6- (or 7)-sulphonic acid (Cleve's acids) and then with 1 mol. of *m*-phenylenediamine. The aqueous solution is violet-black, and is precipitated by acids or alkalis. Solution in strong sulphuric acid is blue, giving a precipitate on dilution.

Literature.—E. P. 12804 of 1900; D. R. P. 131986, 131987; A. P. 679221.

Direct Black BMP (P.) has the same or a very similar constitution, and dyestuffs belonging to the same class are **Carbon Blacks AW, CW, CDW, Naphthamine Direct Blacks FF, B, FG** and **CS** (K.) and **Dianol Blacks FF and FB** (Lev.).

Titan Black J (H.):

$$N_2\begin{cases}C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2\\ C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_6H_3(NH_2)_2.\end{cases}$$

p-Aminoacetanilide is diazotised and combined with 6-amino-α-naphthol-3-sulphonic acid (J acid), the product saponified, tetrazotised, and combined with 1 mol. each of α-naphthylamine-6-(or 7)-sulphonic acid (Cleve's acids) and *m*-phenylenediamine.

Oxydiamine Black N (C.):

$$N_2\begin{cases}C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2\\ C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_6H_3(NH_2)_2.\end{cases}$$

Prepared like Columbia black FB, except that 7-amino-α-naphthol-3-sulphonic acid (γ-acid) is used instead of Cleve's acid. Blue-black aqueous solution gives a black-violet precipitate with hydrochloric acid, and a red-violet one with sodium hydroxide. Solution in strong sulphuric acid is greenish-blue, giving a violet-black precipitate on dilution.

Literature.—A. P. 526763.

Isodiphenyl Black (G.):

$$N_2\begin{cases}C_6H_4\cdot N_2\cdot C_6H_3(OH)_2\\ C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_6H_3(NH_2)_2.\end{cases}$$

Prepared as Columbia black FB, except that resorcinol is used instead of Cleve's acid. Violet-black aqueous solution gives a black precipitate with acids or alkalis. Solution in strong sulphuric acid is blackish-blue, giving a black precipitate on dilution.

Literature.—E. P. 20278 of 1897; F. P. 270151; A. P. 615497.

Direct Black V (K. S.):

$$N_2\begin{cases}C_{10}H_3(SO_3H)_2(OH)\cdot N_2\cdot C_{10}H_6\cdot NH_2\\ C_{12}H_8\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2.\end{cases}$$

7-Amino-α-naphthol-3:6-disulphonic acid (2 R-acid) is diazotised and combined with 1 mol. of α-naphthylamine in acid solution. The mono-azo- dyestuff is then dissolved by adding sodium hydroxide and tetrazotised benzidine added, the combination being effected in presence of sodium carbonate. To this intermediate product is then added 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid). Violet-black aqueous solution gives a blue-black precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in strong sulphuric acid is blue, giving a blue-black precipitate on dilution.

Literature.—E. P. 15294 of 1896; D. R. P. 109161; F. P. 256950; A. P. 601033.

Direct Indone Blue R (K. S.):

$$N_2\begin{cases}C_{10}H_3(SO_3H)_2(OH)\cdot N_2\cdot C_{10}H_6\cdot NH_2\\ C_{12}H_8\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2.\end{cases}$$

Prepared as the preceding, except that 8-amino-α-naphthol-3:6-disulphonic acid (H-acid) is used as the end-component. Blue-black aqueous solution gives a dark-blue precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. Solution in strong sulphuric acid is blue, giving a dark-blue precipitate on dilution.

References as above.

Diamine Bronze G (C.):

$$N_2\begin{cases}C_{10}H_3(SO_3H)_2(OH)\cdot N_2\cdot C_6H_3(NH_2)_2\\ C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH.\end{cases}$$

The dyestuff from tetrazotised benzidine and 1 mol. each of salicylic acid and 8-amino-α-naphthol-3:6-disulphonic acid (H-acid) is diazotised and combined with 1 mol. of *m*-phenylenediamine. The chocolate-brown aqueous solution gives a purple-brown precipitate with hydrochloric acid, and becomes yellower with sodium hydroxide. Solution in strong sulphuric acid is bluish-violet, giving a black precipitate on dilution.

Literature.—E. P. 6972 of 1891; D. R. P. 75762; F. P. 201770.

Trisulphone Browns B, G and **2 G** (K. S.). These are constituted similarly to the preceding, except that a non-specified diamine is used and 7-amino-α-naphthol-3:6-disulphonic acid (2 R-acid) is employed instead of H-acid. (The

diamines used are probably benzidine, tolidine, and dianisidine.) Mark B gives a brown solution in water, which yields a blackish-brown precipitate with hydrochloric acid, and becomes red with sodium hydroxide. The solution in strong sulphuric acid is bluish-violet, giving a dark-brown precipitate on dilution.

Literature.—E. P. 5746 of 1898; D. R. P. 114638; F. P. 275733; A. P. 608024.

Chlorazol Deep Brown B (H.):

$$N_2\begin{cases}C_{10}H_3(SO_3H)_2(OH)\cdot N_2\cdot C_7H_5(NH_2)_2\\ C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH.\end{cases}$$

Benzidine is tetrazotised and combined with 1 mol. each of salicylic acid and 7-amino-α-naphthol-3 : 6-disulphonic acid (2 R-acid), the product being diazotised and combined with *m*-tolylenediamine.

Columbia Black R (A.):

$$N_2\begin{cases}C_{10}H_3(SO_3H)_2(OH)\cdot N_2\cdot C_7H_5(NH_2)_2\\ C_{14}H_{12}\cdot N_2\cdot C_7H_5(NH_2)_2.\end{cases}$$

Tolidine is tetrazotised and combined with 1 mol. each of 7-amino-α-naphthol-3 : 6-disulphonic acid (2 R-acid) and *m*-tolylenediamine, and the product is diazotised and combined with *m*-tolylenediamine. Brown-black aqueous solution gives a black precipitate with hydrochloric acid, and becomes brown with sodium hydroxide. Solution in strong sulphuric acid is pure blue, giving a violet-black precipitate on dilution.

Literature.—E. P. 14895 of 1893; D. R. P. 108215.

Columbia Black B (A.); **Titan Black M** (H.). Prepared as the preceding, except that dianisidine is used instead of benzidine. The violet-black aqueous solution gives a dark flocculent precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in strong sulphuric acid is blue-black, giving a violet-black precipitate on dilution.

Literature.—E. P. 14895 of 1893; D. R. P. 111744.

Columbia Blacks 2 BX and **2 BW** (A.) belong to the same class.

Benzo Black Blue G (By.):

$$N_2\begin{cases}C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ C_{12}H_6(SO_3H)_2\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.\end{cases}$$

Benzidinedisulphonic acid is tetrazotised and combined with 1 mol. of α-naphthylamine, the product diazotised and combined with 2 mols. of α-naphthol-4-sulphonic acid. The blue-black aqueous solution gives a black-blue precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. The solution in strong sulphuric acid is blackish-green, giving a blackish-blue precipitate on dilution.

Literature.—E. P. 16484 of 1887.

Benzo Black Blue 5 G (By.). As the preceding, except that 1 : 8-dihydroxynaphthalene-4-sulphonic acid is used instead of α-naphthol-4-sulphonic acid. The blackish-blue aqueous solution gives a dark greenish-blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is black-green, giving a dark greenish-blue precipitate on dilution.

Columbia Green (A.); **Direct Green CO** (L.):

$$\begin{array}{l}N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH\\ \quad|\\ C_{10}H_3(SO_3H)(OH)\cdot NH_2\\ \quad|\\ N_2\cdot C_6H_4\cdot SO_3H.\end{array}$$

Benzidine is tetrazotised and combined with 1 mol. of salicylic acid, and the intermediate product is combined in alkaline solution with the product of the action of diazotised sulphanilic acid on 8-amino-α-naphthol-5-sulphonic acid (S-acid) in acid solution. The green aqueous solution gives a green precipitate with hydrochloric acid, and becomes greenish-black with sodium hydroxide. The solution in strong sulphuric acid is blue-violet, giving a green precipitate on dilution.

Diamine Green B (C.); **Dianol Green B** (Lev.); **Renol Green B** (T. M.); **Direct Green BN** (P.); **Azidine Green 2 B** (C. J.):

$$\begin{array}{l}N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_4\cdot OH\\ \quad|\\ C_{10}H_2(SO_3H)_2(OH)\cdot NH_2\\ \quad|\\ N_2\cdot C_6H_4\cdot NO_2.\end{array}$$

Prepared in a similar manner as the preceding. Tetrazotised benzidine is combined with 1 mol. of phenol and the product is combined with the azo- colour from diazotised *p*-nitroaniline and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). Dull-green aqueous solution gives a bluish-black precipitate with hydrochloric acid, and becomes yellower with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a black precipitate on dilution.

Literature.—E. P. 15725 of 1891; D. R. P. 66351; F. P. 201770; A. P. 514599.

Diamine Green G (C.); **Chlorazol Green G** (H.); **Dianol Green G** (Lev.); **Azidine Green 2 G** (C. J.).—Prepared as the preceding, except that salicylic acid is used instead of phenol.

Reactions and literature as above.

Diphenyl Green G (G.). Prepared like diamine green B (above), except that *o*-chloro-*p*-nitroaniline is used instead of *p*-nitroaniline. The reactions are also similar to those given by this colour.

Literature.—A. P. 710693.

Diphenyl Green 3 G (G.). Prepared like diamine green G, *o*-chloro-*p*-nitroaniline being used instead of *p*-nitroaniline. The green aqueous solution gives a green precipitate with hydrochloric acid, and becomes duller with sodium hydroxide. Solution in strong sulphuric acid is reddish-violet, giving a green precipitate on dilution.

Reference as the preceding.

Chloramine Green B (K. S.). Benzidine is tetrazotised and combined with 1 mol. of either phenol or salicylic acid, and the product combined in alkaline solution with the azo- colour from diazotised dichloroaniline and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) (combined in acid solution). The green aqueous solution gives a violet-black precipitate with hydrochloric acid, and becomes black-green with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a violet-black precipitate on dilution.

Literature.—E. P. 8503 of 1899; D. R. P. 112820; F. P. 287971; A. P. 627679.

Chloramine Blue HW (K. S.):

$$\begin{array}{l}N_2\cdot C_{12}H_8\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2\\ \quad|\\ C_{10}H_2(SO_3H)_2(OH)\cdot NH_2\\ \quad|\\ N_2\cdot C_6H_3Cl_2.\end{array}$$

Prepared as the preceding, except that 8-amino-α-naphthol-5-sulphonic acid (S-acid) is used instead of phenol or salicylic acid.

Chloramine Blue 3 G (K. S.):

$$\begin{array}{l} N_2\cdot C_{12}H_8\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2 \\ | \\ C_{10}H_2(SO_3H)_2(OH)\cdot NH_2 \\ | \\ N_2\cdot C_6H_3Cl_2. \end{array}$$

Tetrazotised benzidine is combined with 1 mol. of 8-amino-α-naphthol-3 : 6-disulphonic acid (H. acid) and then with 1 mol. of H-acid to which has been added 1 mol. of diazotised dichloroaniline in acid solution.

References for the last two colours as for chloramine green B.

Diamine Black HW (C.); **Ingrain Black G** (H.); **Naphthamine Black H** (K.):

$$\begin{array}{l} N_2\cdot C_{12}H_8\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2 \\ | \\ C_{10}H_2(SO_3H)_2(OH)\cdot NH_2 \\ | \\ N_2\cdot C_6H_4\cdot NO_2. \end{array}$$

Prepared like diamine green B (above), except that 7-amino-α-naphthol-3-sulphonic acid (γ-acid) is used instead of phenol. Blackish-blue aqueous solution gives a blue precipitate with hydrochloric acid. Solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 15725 of 1891; D. R. P. 66351, 70399; F. P. 201770; A. P. 514599.

Dianil Black R (M.):

$$\begin{array}{l} N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(NH_2)_2 \\ | \\ C_{10}H_2(SO_3H)_2(OH)_2 \\ | \\ N_2\cdot C_{10}H_6\cdot SO_3H. \end{array}$$

Tetrazotised benzidine is combined with 1 mol. of *m*-phenylenediamine and then with 1 mol. of 1 : 8 - dihydroxynaphthalene-3 : 6 - disulphonic acid (chromotrope acid), to which has been added 1 mol. of diazotised naphthionic acid. The reddish-violet aqueous solution gives a precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in strong sulphuric acid is dark blue, giving a reddish-violet precipitate on dilution.

Literature.—D. R. P. 89285.

Congo Brown G (A.); **Naphthamine Brown 4G** (K.):

$$\begin{array}{l} N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH \\ | \\ C_6H_2(OH)_2 \\ | \\ N_2\cdot C_6H_4\cdot SO_3H. \end{array}$$

The dyestuff from tetrazotised benzidine, salicylic acid and resorcinol is treated with diazotised sulphanilic acid or the intermediate product from tetrazotised benzidine and 1 mol. of salicylic acid is combined with 1 mol. of resorcinol to which 1 mol. of diazotised sulphanilic acid has been added. The red aqueous solution gives a brown precipitate with hydrochloric acid. Solution in strong sulphuric acid is reddish-violet, giving a reddish-brown precipitate on dilution.

Literature.—E. P. 10653 of 1888; D. R. P. 46328, 46501; F. P. 192331; A. P. 399581.

Congo Brown R (A.):

$$\begin{array}{l} N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH \\ | \\ C_6H_2(OH)_2 \\ | \\ N_2\cdot C_{10}H_6\cdot SO_3H. \end{array}$$

Prepared as the preceding, except that α-naphthylamine-5-sulphonic acid (Laurent's acid) is used instead of sulphanilic acid. Reactions and references as the preceding.

Azo Corinth (O.):

$$\begin{array}{l} N_2\cdot C_{14}H_{12}\cdot N_2\cdot C_6H_2(SO_3H)(OH)\cdot NH_2 \\ | \\ C_6H_2(OH)_2 \\ | \\ N_2\cdot C_{10}H_6\cdot SO_3H. \end{array}$$

Tetrazotised tolidine is combined with 1 mol. of 3-aminophenol-6-sulphonic acid (acid III.) and 1 mol. of resorcinol, and the colouring matter so obtained is treated with 1 mol. of diazotised naphthionic acid. Reddish-brown aqueous solution gives a reddish-brown precipitate with hydrochloric acid, and is turned bluish-red with sodium hydroxide. Solution in strong sulphuric acid is bluish-violet, giving a reddish-brown precipitate on dilution.

Literature.—E. P. 13402 of 1893; D. R. P. 71182; A. P. 516381.

V. Tetrakisazo- Colouring Matters.

These contain four azo- groups.

Benzo Brown G (By.):

$$C_6H_4\begin{cases} N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_6H_4\cdot SO_3H \\ N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_6H_4\cdot SO_3H. \end{cases}$$

Prepared by the action of diazotised sulphanilic acid (2 mols.) on Bismarck brown (1 mol.). Reddish-brown aqueous solution gives a brown precipitate with acids and alkalis. Solution in strong sulphuric acid is violet-brown, giving a brown precipitate on dilution.

Literature.—E. P. 16493 of 1887; D. R. P. 46804; A. P. 384315.

Benzo Brown B (By.):

$$C_6H_4\begin{cases} N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H \\ N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H. \end{cases}$$

Prepared as the preceding, except that naphthionic acid is used instead of sulphanilic acid. Reactions and references as above.

Toluylene Brown R (O.) (By.); **Azidine Brown T 2 R** (C. J.):

$$HSO_3\cdot C_7H_5\begin{cases} N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H \\ N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H. \end{cases}$$

Prepared by treating the colour from tetrazotised 2 : 6-tolylenediamine-4-sulphonic acid and 2 mols. of *m*-phenylenediamine with 2 mols. of diazotised naphthionic acid. Brown aqueous solution gives a brown precipitate with hydrochloric acid. Solution in strong sulphuric acid is dull reddish-violet.

Literature.—E. P. 11000 of 1889; D. R. P. 58657; A. P. 465116.

Hessian Brown BB (L.):

$$C_{12}H_8\begin{cases} N_2\cdot C_6H_2(OH)_2\cdot N_2\cdot C_6H_4\cdot SO_3H \\ N_2\cdot C_6H_2(OH)_2\cdot N_2\cdot C_6H_4\cdot SO_3H. \end{cases}$$

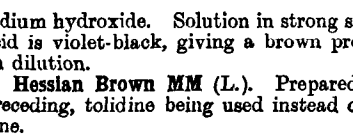
Prepared by the action of tetrazotised benzidine on 2 mols. of the monoazo- dyestuff from diazotised sulphanilic acid and resorcinol. Aqueous solution is brown, giving a brown precipitate with hydrochloric acid, and becoming red with

sodium hydroxide. Solution in strong sulphuric acid is violet-black, giving a brown precipitate on dilution.

Hessian Brown MM (L.). Prepared as the preceding, tolidine being used instead of benzidine.

Reactions as above.

Mekong Yellow G (D. H.):



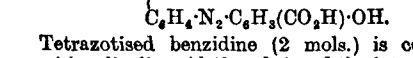
Tetrazotised benzidine (2 mols.) is combined with salicylic acid (2 mols.) and the intermediate product is combined with dihydroxydiphenylmethane (1 mol.). Yellowish-brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes reddish-brown with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a brown precipitate on dilution.

Literature.—E. P. 8511 of 1893; D. R. P. 80816; F. P. 228593; A. P. 519523.

Mekong Yellow R (D. H.). Prepared as the preceding, but tolidine is used instead of benzidine.

Reactions and literature as above.

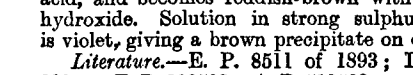
Cuba Black (Petersen); **Dianil Black** (M.):



Benzidinesulphonic acid is tetrazotised and combined with 2 mols. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) in alkaline solution, and the product is tetrazotised and combined with 2 mols. of *m*-phenylenediamine. Black aqueous solution is precipitated with hydrochloric acid or sodium hydroxide. Solution in strong sulphuric acid is dark-blue, giving a black precipitate on dilution.

Literature.—E. P. 13743 of 1896; F. P. 257245; A. P. 578580.

Anthracene Acid Brown B (C.):



Nitroaminosalicylic acid is diazotised and combined with α-naphthylamine. Two mols. of this are diazotised and combined with 1 mol. of *m*-phenylenediamine. Brown aqueous solution gives a violet precipitate with hydrochloric acid. Solution in strong sulphuric acid is greyish-violet, giving a brown-violet precipitate on dilution.

Literature.—E. P. 2446 of 1896; D. R. P. 92655. J. C. C.

AZO- ACID YELLOW, -ALIZARIN YELLOW, -BLACK BASE O, -BORDEAUX, -CHROMINE, -COCCINE, -COCHINEAL, -CORALLINE, -EOSINE, -FLAVINE, -FUCHSINES (*v.* AZO- COLOURING MATTERS).

AZOERYTHRIN *v.* ARCHIL.

AZOFLAVIN *v.* AZO- COLOURING MATTERS.

AZOGEN RED *v.* AZO- COLOURING MATTERS.

AZOGRENADINES *v.* AZO- COLOURING MATTERS.

AZOIMIDES, AROMATIC *v.* DIAZO COMPOUNDS.

AZOLITMIN. A substance assumed by Kane to exist in litmus (Annalen, 39, 25).

AZOMETHANE *v.* DIAZO COMPOUNDS.

AZOORSEILLIN *v.* AZO- COLOURING MATTERS.

AZOPHENYLENE *v.* AZINES.

AZOPHOR -BLACK, -BLUE, -RED, -ROSE *v.* AZO- COLOURING MATTERS.

AZOPHOSPHINES *v.* AZO- COLOURING MATTERS.

AZO-REDS, AZORUBINES *v.* AZO- COLOURING MATTERS.

AZOTE. A name given to nitrogen by Lavoisier, and hence commonly used in French literature to designate that element.

AZOTINE. An explosive made in Austria-Hungary (J. Soc. Chem. Ind. 4, 366).

AZOTOL *v.* AZO- COLOURING MATTERS.

AZOTOMETER. A term applied by W. Knop to an apparatus designed to measure the nitrogen evolved by the action of sodium hypochlorite or hypobromite on ammonium salts and certain organic substances.

AZO- TURKEY RED *v.* AZO- COLOURING MATTERS.

AZO-VIOLET *v.* AZO- COLOURING MATTERS.

AZOXINE COLOURING MATTERS *v.* OXAZINE COLOURING MATTERS.

AZOXYBENZENE $C_{12}H_{10}N_2O$. A product of the partial reduction of nitrobenzene with alcoholic potash (Zinin, J. pr. Chem. 36, 93; Schmidt and Schultz, Annalen, 207, 325; Ber. 12, 484); or with sodium amalgam containing 3·8 p.c. of sodium (Alexejeff, J. 1864, 525; Moltschanowsky, Ber. 15, 1575).

Preparation.—Azoxybenzene is best prepared by dissolving 1 part of sodium in 25 parts of methyl alcohol, adding 3 parts of nitrobenzene and heating for 5 or 6 hours on a water-bath in a flask provided with a reversed condenser. The methyl alcohol is then distilled off and the residue treated with water, which dissolves the sodium formate formed in the reaction, and leaves the azoxybenzene as a yellow oil; this soon solidifies, and is obtained pure by one crystallisation from alcohol (Klinger, Ber. 15, 866; Moltschanowsky, *l.c.* and Ber. 16, 81; Klinger, Ber. 16, 941, footnote).

Azoxybenzene is also prepared by the reduction of nitrobenzene with arsenious oxide and caustic soda (Loesner, Eng. Pat. 1555, J. Soc. Chem. Ind. 1895, 31); by the reduction of nitrobenzene with alkali sulphides in alkali hydroxide, the products being mainly azoxybenzene and azobenzene, in proportions varying with the amount of sulphide and the time of reduction (Farb. vorm. Meister, Lucius, and Bruning, D. R. P. 216246, J. Soc. Chem. Ind. 1909, 1310); by boiling nitrobenzene with 60 p.c. aqueous sodium hydroxide and iron pyrites, or other heavy sulphides, 90 p.c. of the product being azoxybenzene (Farbenfab. vorm. Fried. Bayer & Co., D. R. P. 204653, Chem. Soc. Abst. 1909, i. 272); by heating nitrobenzene with charcoal and alkali (Farbenfab. vorm. Fried. Bayer & Co., D. R. P. 210806; Chem. Zentr. 1909, ii. 163); and by the electrolytic reduction of nitrobenzene in the presence of alkali (Farb. vorm. Meister, Lucius, and Bruning, D. R. P. 127727; Chem. Zentr. 1902, i. 446, and Farb. vorm. Weiler-ter-Meer, D. R. P. 138496; Chem. Zentr. 1903, i. 372).

Azoxybenzene or its homologues can be obtained by heating nitrobenzene or the corresponding nitro- compound with an equal weight of zinc-dust and of an aqueous solution of calcium chloride boiling at 130°; aqueous solutions

of other salts may be employed, and the reaction ensues at the boiling-point of the aqueous solution (*v.* Dechend, D. R. P. 43230.

Properties.—Azoxybenzene crystallises in pale yellow rhombic needles, melts at 36°, and is soluble in alcohol or ether, insoluble in water. When heated with non-volatile substances, such as iron filings, it decomposes into aniline and azobenzene. Weak reducing agents, such as sodium amalgam in alcoholic solution, convert it into hydrazobenzene (Alexejeff, J. 1867, 503); but more powerful agents, such as zinc chloride in acid solution, reduce it chiefly to aniline, a small quantity of hydrazobenzene and bases derived from it by molecular changes being also formed (Schmidt and Schultz). Azoxybenzene yields two isomeric nitroazoxybenzenes when heated with concentrated nitric acid (Linin, Annalen, 114, 217), and when heated with concentrated sulphuric acid to a moderate temperature is converted into the isomeric hydroxyazobenzene (Wallach and Kiepenheuer, Ber. 14, 2617).

In addition to azoxybenzene other azoxy-compounds have been prepared by reducing the corresponding nitro- derivatives either with sodium amalgam in methyl alcohol solution or with zinc-dust and soda (*cf.* Limpricht, Ber. 18, 1405; Klinger and Pitschke, Ber. 18, 2553; Janovsky and Reimann, Ber. 22, 41; *v.* Dechend, *l.c.*). The azoxy- compounds derived from metanitraniline, the nitrotoluidines melting at 78° and 107°, and the nitroxylidine melting at 123° yield, when diazotised and combined with phenols, amines or their sulphonic acids, a class of yellow, orange or red azo- dyes, which can be employed for cotton and wool (Poirrier and Rosenstiehl, D. R. P. 44045, 44554).

AZOXY- COLOURING MATTERS. The dyes formerly classified under this heading, of which 'sun yellow' is perhaps the best known, have been shown to be azo- dyes (*q.v.*).

AZO-YELLOWS *v.* AZO- COLOURING MATTERS.

AZULIN. Blue colouring matter, contained in certain essential oils; *e.g.* chamomile, millefolium, and wormwood.

AZULIN or **AZURIN** *v.* AURIN.

AZURE *v.* PIGMENT.

AZURIN $C_{35}H_{32}N_4O_3$. Obtained by heating salicylic aldehyde with *o*-tolylenediamine. Colourless tables, giving blue fluorescent solutions (Ladenberg, Ber. 11, 596).

AZURITE *v.* LAZULITE and COPPER.

AZURITE or Chessylite. Hydrated basic copper carbonate, $2CuCO_3{\cdot}Cu(OH)_2$, forming monoclinic crystals of an azure-blue colour. Finely crystallised specimens have been found in abundance in an old copper mine at Chessy, near Lyon in the south of France, and on this account the mineral is often known as chessylite (Brooke and Miller, 1852); the name azurite (F. S. Beudant, 1824) refers to the characteristic colour. Sp.gr. 3·8; hardness 3½–4. It occurs as an alteration product of copper-pyrites and other sulphide ores of copper in the upper oxidised zones of mineral veins; and it is itself often altered to malachite, the green carbonate ($CuCO_3{\cdot}Cu(OH)_2$). Fine crystals are found at Broken Hill in New South Wales and at Bisbee in Arizona; at the latter place it occurs, together with malachite, in sufficient abundance to be mined as an ore of copper. It was also formerly mined at Burra-Burra, in South Australia. From Arizona come pretty specimens, with azurite and malachite banded together, which are polished for use in cheap jewellery. Powdered azurite was formerly used as a pigment under the name 'mountain blue,' but this is now replaced by an artificial product.

L. J. S.

B

BABBIT'S METAL. An alloy of 25 parts tin, 2 parts antimony, and 0·5 part copper, used as an anti-attrition metal (*v.* ANTIMONY).

BABLAH or **NEB-NEB.** Commercial names for fruits of several species of acacia; used in the East, in combination with alumina and iron mordants, to produce various shades of drab and fawn colour in calico-printing. East Indian bablah is largely obtained from *Acacia arabica* (Willd.) (*A. indica* (Benth.)); Senegal and Egyptian bablah largely from *Acacia arabica* (*A. nilotica* (Delil.)). The aqueous extracts contain a red colouring matter together with considerable quantities of gallic and tannic acids.

BAPTISIN *v.* GLUCOSIDES.

BABUL BARK. The bark from *Acacia arabica* (Willd.) which occurs in India, Arabia, and tropical Africa: its Indian vernacular name is 'babul.' Used in India as a tanning material.

BABUL GUM. An inferior kind of gum arabic from *Acacia arabica* (Willd.). Known also as 'Bengal gum' or 'Gond babul.'

BACTERIA, CHEMICAL ACTION OF, *v.* FERMENTATION.

BAEL FRUIT. The dried half-ripe fruit of *Ægle Marmelos* (Correa), from Malabar and Coromandel; is used in diarrhœa and dysentery, and the fresh pulp is sometimes employed as a laxative.

BAGASSE, BEGASS, or MEGASS. Terms applied to the refuse sugar-cane after crushing.

BAKING POWDERS are any powders used as substitutes for yeast. The bread or cake is rendered spongy by the carbon dioxide generated in the dough; this is effected by the action of an acid, such as tartaric acid, on sodium bicarbonate, and some farinaceous substance is added to act as diluent. To permit the use of discoloured flour, alum was requently employed, this renders the bread white, but at the same time indigestible. In 1899 such articles as baking powder were included in the Sale of Food and Drugs Acts, and therefore the use of alum or any injurious matter was prohibited. All articles are perfectly dried before mixing, passed through a fine sieve, and kept in air-tight packages in a dry place. To every pound of flour, 1 teaspoonful of baking powder is added for bread, and 2 teaspoonfuls for cakes. General preparations are:

(1) 6 ozs. tartaric acid, 2 ozs. sodium bicarbonate, and 1·5 ozs. of farina.

(2) 16 ozs. sodium bicarbonate, 14 ozs. tartaric acid, and 6 ozs. magnesium carbonate, and 12 ozs. farina (Workshop Receipts, 1909).

(3) 2½ lbs. cream of tartar, 2½ lbs. sodium bicarbonate, 1 lb. acid calcium phosphate, and 4 lbs. cornflour (Pharm. Formulæ, 1908, p. 322).

(4) 3 lbs. acid potassium sulphate, 1 lb. sodium bicarbonate, and 1 lb. of cornflour (Pharm. Formulæ, 1908, p. 322).

(5) 5 ozs. tartaric acid, 15 ozs. cream of tartar, 20 ozs. sodium carbonate, and 40 ozs. rice flour (Workshop Receipts, 1909, p. 90).

(6) 20 parts acid sodium phosphate, 20 parts acid calcium phosphate, 25 parts sodium bicarbonate, and 35 parts starch (Hiscox, 1907, 102).

Crampton's powder: 2 parts cream of tartar, 1 part sodium bicarbonate, and 1 part corn starch.

Rumford's powder: (approx.) 7 ozs. sodium bicarbonate, 14½ ozs. sodium phosphate, and 3½ ozs. starch.

Royal powder: A mixture of cream of tartar, tartaric acid, sodium bicarbonate, and starch.

Goodall's powder is a mixture of 2 parts rice flour with 1 part tartaric acid and 1 part bicarbonate of soda.

Green's powder: 35 lbs. tartaric acid, 56 lbs. of sodium carbonate, and 1 cwt. of potato flour.

Horsford's powder consists of 2 packets: (1) acid calcium and magnesium phosphates, made up with a certain quantity of flour; (2) bicarbonate of soda with a little potassium chloride.

Borwick's powder is an artificial fermentation powder compounded with coarse maize.

Self-raising flour may be prepared by mixing 8 ozs. sodium bicarbonate, and 18 ozs. cream of tartar with 1 cwt. of flour.

Milk in the solid form, concentrated in a vacuum at 50°–60°, was used by Hooker, to replace inert farinaceous matter. It is claimed to have a better nutriment value and increased leavening power: 20 parts tartaric acid, 54 parts milk powder, and 1 part moisture. The soda is added before the milk is completely dry, then the whole dried and ground finely in a mortar (J. Soc. Chem. Ind. 27, 1908). Cream of tartar is soluble in hot water, but only slightly so in cold, whilst tartaric acid dissolves readily. Therefore a powder containing cream of tartar evolves carbon dioxide much more slowly than one compounded with tartaric acid. This is advantageous, as a dough containing it can be kept for some time before baking, also it does not darken the bread; on the other hand, it forms Rochelle salt which has a very slight saline taste. The best powders are made from a mixture of tartaric acid and cream of tartar. Good substitutes for tartaric acid are acid ammonium phosphate, and acid potassium sulphate, acid potassium and calcium phosphates, but they have a tendency to darken the bread.

Ammonium carbonate is used in very light pastries, but it requires expert handling, and so is very rarely present in the made-up preparations.

BAKUIN. Russian mineral machine oils; recommended for lubricating heavy machinery on account of their high viscosity and great power of resisting cold (Seifenseid, Zeit. 31, 366; 32, 378; J. Soc. Chem. Ind. 3, 181).

BAKUOL. A name given by Mendeléeff to an illuminating oil, prepared from the crude oils of Baku by mixing ordinary kerosene of sp.gr. 0·82 to 0·83 and flashing point 20° to 30°, with the so-called intermediate oil, which has a sp.gr. of 0·86 to 0·88 at 15°, and is not inflammable at 100°. The mixture has a sp.gr. of 0·84 to 0·86, and flashes at temperatures varying from 50° to 70°. From 100 parts crude naphtha 20 to 30 parts of kerosene and 10 to 20 parts of intermediate oil can be obtained.

The following table gives the sp.gr., flashing-point, and luminiferous value of four bakuols examined by Ilimow:—

Specimen of oil	Sp. gr. at 17°·5	Flashing point at 760 mm.	Candle-power	Consumption per hour in Russian lbs.	
				For the lamp	Per candle power
No.					
1	0·8280	38°·0	7·40	0·0588	0·0080
2	0·8310	37·5	10·40	0·0633	0·0060
3	0·8360	39·5	9·84	0·0633	0·0064
4	0·8310	49·5	8·30	0·0675	0·0081

Literature.—Mendeléeff, Zeitschr. Technik, 1886, No. 109; Chem. Zeit. 1883, 231; Ilimow, *ibid.* 10, 1459; J. Soc. Chem. Ind. 2, 238; 5, 661; 6, 135 (*v.* PETROLEUM, RUSSIAN).

BAKURIN. A lubricating oil, prepared by mixing 100 parts of crude Baku oil with 25 parts of castor oil and 60 to 70 parts of sulphuric acid of 66°B. After standing the mixture is stirred two or three times with water, the water run off, and the oil treated with soda or potash (Müller, D. R. P. 35141, Dingl. poly. J. 260, 240).

BALANCE. A generic term, designating a variety of machines for ascertaining the weight of a body in terms of the weight, at the time and place, of a standard *mass* (gram, ounce, pound, &c.), and thus determining its mass. By means of a balance and a set of 'weights,' we ascertain that a body has P times the weight of the unit piece of the set, and conclude that its mass is P times the mass of this piece likewise, whatever the chemical nature of the body may be. In justification of this inference we might refer to Newton's pendulum experiments, or to the often proved chemical axiom that the weight of any body or set of bodies is independent of the state of combination of its elements. But from the standpoint of the chemist it is sufficient to know that, supposing even each element had its own factor for converting 'weight' into mass, it would still follow that the weight of a body, however complex, is equal to the sum of the weights of what in any sense we may call its 'components,' and that the ratio of the weight W_1 of a body of fixed elementary composition to the weight W_2 of another body of even a different fixed composition is as constant, although perhaps not equal to the ratio of the masses $M_1 : M_2$. Of all balances the equal-armed lever balance, often called '*the* balance' *par excellence*, is by far the most important.

The balance exists in a variety of forms, all of which seek to realise the same ideal

machine.' An absolutely rigid beam, so suspended that whilst it can rotate freely about a certain axis (which goes across it somewhere above its centre of gravity, and of which every point holds a fixed position in reference to the stand) it is not capable of any other motion. From two points, *a* and *b*, which lie in the same plane as the axis of rotation—one near the left, the other near the right end of the beam—the pans are suspended by means of absolutely flexible linear strings. *a* and *b* are equidistant from the axis of rotation. So far all balances are alike. In now passing to the actual instrument, we shall confine ourselves in the main to the class of balances known as precision balances.

Of the difficulties involved in the construction of such balances, that of producing a sufficiently light and yet practically inflexible beam seems to have rested most heavily on the minds of the earlier makers; but there can be no doubt that many of their efforts in this direction, which occasionally resulted in what we should now call fantastical beam-forms (hollow ellipsoids, monstrous skeleton-forms, &c.), must be traced back to their inability to reach a sufficient degree of precision in the geometric adjustment of the three pivots, and to their charging against the flexibility of the beam what was really owing to these defects in the adjustment. As these difficulties were overcome, beams assumed less fantastic forms. Sacré of Brussels, we believe, never uses any but plain rod-shaped beams (only perforated in the middle to insert the bearing of the central knife). Most balance makers, however, prefer the form of a largely perforated rhombus or isosceles triangle (cut out, virtually, of a plate of metal), and thus attain all that is needful without offending the eye by unduly stretching the middle section, and without using anything more intrinsically rigid than hammered brass or some kind of bronze. In reference to ordinary chemical balances (for charges up to say 100 grams), it would be no great exaggeration to say that any reasonably made beam is sufficiently rigid; only in the case of balances intended for very high charges, such as 5–10 kilogrammes, is it at all worth while to employ refinedly designed beam-forms, or to look out for a material of exceptionally high rigidity. For these particular balances hard steel would be the best material; but, unfortunately, steel beams are apt to become magnetic. With small assay-balances intended for charges up to, say, 5 grams, on the other hand, the question of rigidity is practically out of court, and the use of an exceptionally light material—such as aluminium, or, better, that alloy of 95 parts of aluminium and 5 of silver (which Sartorius of Göttingen uses for small balances generally) is indicated.[1] In all balances the axis of rotation is realised in a straight knife-edge ground to a prism of hard material, which is firmly fixed to the beam, traversing it crosswise and resting on a hard bearing. In ordinary balances the middle knife is simply driven through the beam, and only its two ends are supported in cylindrical, or, what is better, roof-shaped bearings, which form secures to the edge a sufficient fixity of position, forward and back sliding being prevented by cutting off the ends of the knife obliquely, so that the edge terminates in two points, and closing the bearing at each end by a steel plate, so that the knife has just room between without jamming. In suspended balances the central bearing is fixed at the lower end of a light framework, terminating above in a hinged-on ring for suspending the instrument from a fixed hook or the thumb of the operator.

In all precision balances the central bearing is attached to a fixed pillar, and is plane; in the best balances the bearing is made of one piece, and the central knife-edge rests upon it in its entire length. A plane bearing necessarily involves an arrestment so constructed that, besides doing its primary duty, it assigns to each point of the central knife-edge a fixed position on its bearing. In former times hard steel was used exclusively for both knives and bearings; subsequently agate bearings came to be combined with steel knives. Robinson of London was the first to make both knives and bearings of agate. The agate knife adds nothing to the precision of a newly-made balance, but it always remains clean, while a steel knife, in a chemical laboratory more especially, is apt to rust. Steel knife-edges are generally ground to an angle of 60° (or 90° for very heavy charges). In agate knives, as made by Oertling, only the body of the agate prism is ground to 60°, while the edge is formed by two narrow facets, inclined to each other at a far more obtuse angle. Such an obtuse edge stands many years' constant use without wearing out. American makers have introduced the artificially made osmium-iridium, which is used for the tipping of stylograph pens, as a material for both knives and bearings.

For the realisation of the two point-pivots A and B, a great many combinations have been invented. A now obsolete construction of Weber's (Bib. 2) adapts itself very closely to our ideal conception. He provides the beam at its two ends with knife-edges turned sideways and suspends the pans by means of threads of unspun silk which are fixed somewhere in the back of the beam and hang over the edge. The axis of rotation is realised similarly. In ordinary balances, as a rule, a vertical slit is cut into each end of the beam, and this is traversed by a short prismatic knife, the edge of which is a circular arc of small radius which stands perpendicular to the line AB. From each such knife the pan is suspended by means of an 8 or 2-shaped steel hook. This construction, if well executed, may afford high precision, but the suspender-hook is apt to rub against the sides of the slit in the beam. Hence, wherever the hook-and-eye arrangement is adopted for precision balances, it is modified in this sense, that the knife-edge forms a circle of relatively large radius which lies entirely outside the body of the beam. This system, compared with those considered in the sequel, offers the advantage of easy adjustment. It used to be very popular with balance makers, and many excellent instruments have been produced with it especially by Deleuil of Paris. For small assay-balances it is indeed probably as good as any other that could be named; for balances intended for higher charges it does not possess sufficient durability, although, as the writer is able to say from his own experience, if well made, it lasts better than is generally supposed. In modern balances it is rarely seen;

[1] For a fuller discussion of this subject, *v.* the writer's Memoir (Bib. 6, 322).

in these, as a rule, the pans are suspended from long straight knife-edges, similar to the central one, by means of broad bearings which, of course, must be arranged so that they neither twist nor slide. A very efficient and easily made arrangement is to give the bearing the form of a roof cut and of one side of a prismatic block of steel or agate, and to fix it to the upper end of a stirrup-shaped or ⅂-shaped holder which terminates below in an eye, from which the pan is suspended by a suitable hook. The eye stands at right angles to the knife-edge; its working point, when the instrument is in use, lies vertically below the centre of the respective end-edge, and the effect is the same as if the whole of the load were concentrated in that one centre-point, although the pressure of the bearing on the knife is equally distributed over the whole of its working length. This hook-and-eye arrangement is absolutely indispensable if the pans are suspended by stiff stirrups, because, if these were rigidly connected with their bearings, the virtual point of application of the load would shift forwards and backwards on the edge, and the least want of parallelism between it and the axis of rotation would cause the balance to give inconstant readings.

These roof-shaped bearings were formerly used almost exclusively by German makers, although an undoubtedly superior system had been introduced successfully by Robinson of London many years ago. In it the pans are suspended by *plane* bearings which a suitable extension of the arrestment keeps in their right positions. Robinson's balances were justly famous in Great Britain—a few of them are still working to this day—yet, after Robinson's death, Oertling was almost the only balance maker who followed him in this respect. The general plea against the system was that flat end-bearings were liable to twist; and some, after having adopted Robinson's plan, 'improved' upon it by cutting out a central portion of each end-knife, so that it worked only with its two ends; proving thereby that they did not understand their business, because a *really plane* bearing, as a matter of fact, does *not* twist on a *really straight* knife-edge, even if the pan oscillates strongly. The principal advantage of the Robinson system is that it enables one to do what the roof-shaped bearing prohibits, namely, to satisfy himself that the knives and bearings are geometrically perfect. But here, as in all analogous cases, we must not forget that the excellence of an instrument—supposing it to be based on a reasonable system—depends far more on the skill of the maker than on the theoretical perfection of the design.

From the bare realisation of the ideal machine, we now pass to the accessories which a balance needs in order to become a convenient instrument, and we will consider these in the order of their importance.

The arrestment is a mechanical contrivance to enable the beam to be arrested at any point of its angular motion, and to bring it to permanent rest in its '*normal*' position, in which the plane of three axes stands horizontal. If the three pivots are self-adjusting, there is, strictly speaking, no need of an arrestment; still for the rapid execution of precise weighings it is almost indispensable.

If the central bearing forms part of a suspended frame, an arrestment is easily devised in the ways illustrated by Figs. 1 and 2. Fig. 1 explains itself; in Fig. 2 the balance is hinged on to the bent-down end of a flat bar which slides up and down in guides fixed to the pillar between two beds of rollers 2×2 in the guides on the front side of the bar, and one which is pressed against its back by a spring. At its lower end the bar has a small wheel which rests on the shorter end of the hinged lever by means of which the balance is raised or lowered. A small vertical adjusting screw below the shorter end of the lever defines the lowest position of the bar at which the pans just touch the table without slackening the chains. In either case it is an improvement to suspend a heavy block of metal at the lower end of the frame, to compel it to hang plumb, and to hinder it from oscillating. The specific advantage of *suspended* balances is that they need no horizontal table or levelling screws at the board on which they may be erected. But pillar-balances are on the whole more convenient. In the case of these (supposing plane bearings to be absent) a good system

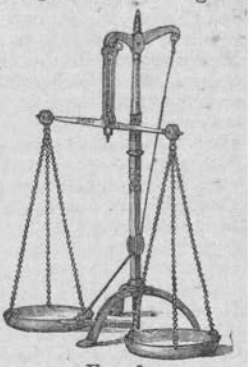


Fig. 1.

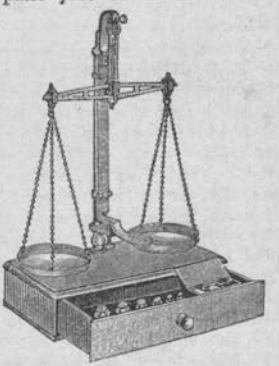


Fig. 2.

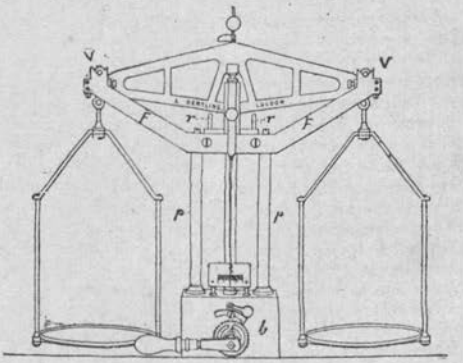


Fig. 3.

is to fix the central bearing to the top of a rod which slides up and down within the pillar—properly guided to prevent shaking and rotatory motion—and, with its lower end, rests on an eccentric concealed in the sole and governed

by a lever- or disc-shaped handle. The eccentric must be so adjusted that when it is at one of its extreme positions, the pans just touch the board and no more, while, when it is in its other extreme position, the beam is at its maximum angle of free play. In the excellent *Tarirwaagen* of Messrs. Becker's Sons, Rotterdam, this system of arrestment is realised to perfection.

The system needs only be slightly modified to adapt itself to the case of a plane central bearing, but we prefer to at once pass to the case of *three* plane bearings, and in doing so cannot do better than describe a balance (for charges up to 5 kilos.) which Mr. Oertling made for us some years ago. As shown by Fig. 3, the instrument rests on three pillars standing on a hollow square block of iron which conceals the eccentric. Firmly fixed to the top ends of the pillars is a substantial brass frame which terminates at its two ends in V-shaped supports for the end-bearings. These latter are agate plates cemented each to the horizontal bar of a kind of stirrup, the bar terminating on each side in a cylindrical steel pin which, when the balance is at rest, lies in the corresponding V of the frame. The central pillar conceals a movable steel rod, provided at its lower end with a wheel which rests on the eccentric. Its upper end carries a substantial brass block which divides into two short piers above, whilst it expands below into a horizontal plate, pierced by a circular perforation near each end. These perforations fit exactly around two cylindrical steel pins, *r*, *r*, fixed to the top plate of the pillars, so that the rod, when moving up or down, cannot turn or shake in the slightest degree. The space between the two piers is bridged over by the central bearing, a plane agate plate fixed to a prismatic piece of brass, which is dovetailed into the tops of the piers, so that, while perfectly steady when in its place, it can without much effort be slid out or in (Fig. 4). It is inserted while the beam is being held in its intended position and passes through a large perforation in the beam into which the middle knife projects. The beam terminates at its left end in one, at its right end in two, horizontal steel pins whose shoulders are continuous but rapidly expanding surfaces of rotation, and these pins fit, the single one into a notch, the couple into a fork, forming part of the fixed arrestment frame. In the arrested balance each bearing is almost in contact with its knife; if the eccentric be now turned, the central bearing rises and lifts the whole, beams and end-bearings, to a greater or less height, and ultimately into that maximum height at which the eccentric stands still without being *held* in its position. If the eccentric be now turned the other way, both the beam and the end-bearings fall back, ultimately, into their prescribed positions of rest, even if they should have twisted, which, however, they never do in the instrument under description. For a balance intended for quick work, and more especially for one used occasionally for the weighing out of predetermined quantities of solids or liquids, this system of arrestment is the best that we know of, because it enables the instrument to be handled pretty much like an ordinary pair of scales; only, to be able to do so to the best advantage, and without spoiling the terminal pivots, the pans must be suspended by flexible short-linked chains whose length is so adjusted that the pans just touch the table when the balance is fully arrested. Stirrup-shaped pan-suspenders (as represented in the figure) are more convenient than chains in many respects, but, for the purpose under consideration, they do not work with plane end-bearings. The ratchet-wheel visible in the figure was intended to enable the eccentric to be arrested at intermediate positions (in taring with garnets and similar operations) but was found not to work satisfactorily; it is simpler and better to have a block of wood so adjusted that when put under the handle it just raises the

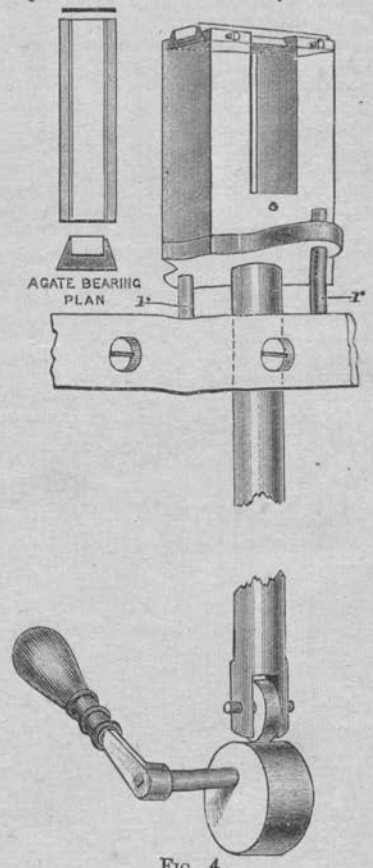


FIG. 4.

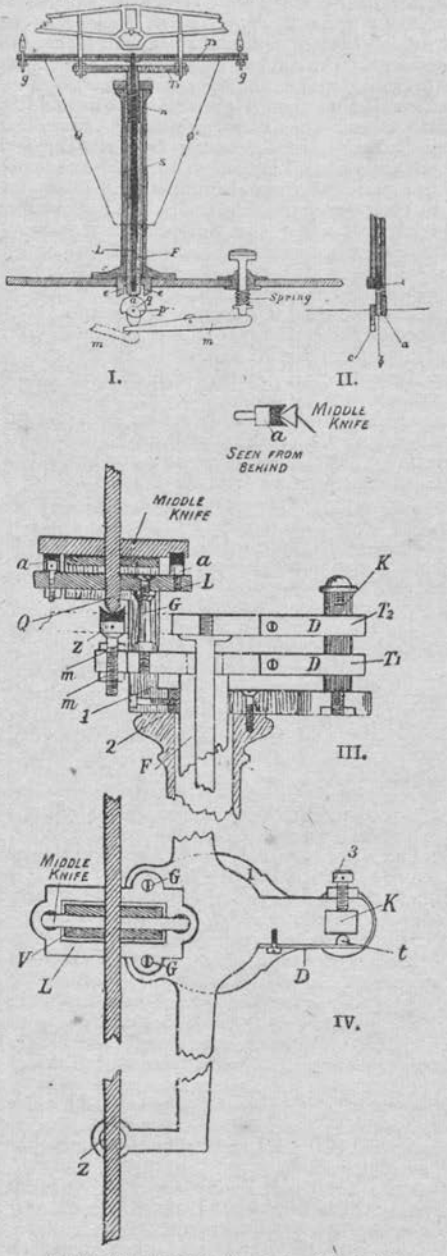
beam sufficiently to enable one to see which side goes down.

Instead of fixing the arrestment frame to the pillar and making the central bearing movable, we may of course do the reverse, and this latter system, indeed, is generally preferred for precision balances of a higher order.

The kindness of Messrs. C. Staudinger's Nachfolger, of Giessen, Germany, enables us to give a detailed description and drawing of the kind of movable frame arrestment which they are in the habit of applying to their best instruments.

As shown by Fig. 5 (I. to IV.) the pillar is hollow and accommodates a round bronze rod F. This rod itself, however, conceals a co-axial

round rod L of nickelled steel. The bronze rod F, at its lower end, is guided by perforated blocks, *e*, *e*, Fig. I., while at its upper end it terminates



III. Section through pillar and middle knife; IV. Horizontal projection.

FIG. 5.

in a thinner cylinder surrounded by a gently acting spiral spring *n*. The head of the pillar is perforated and guides the attenuated end of F in its up-and-down motion. The inner (steel) rod, L, is guided similarly within the bronze rod F and has a spring *i*, Fig. II., about its lower end to assist its natural tendency to sink. The two rods F and L carry two independent arrestment-bars; L the bar T_2 for the end-bearings, F the bar T_1 for the beam.

A square pillar K (Figs. III. and IV.), which rises from a prolongation of the head of the stand pillar S, by passing through perforations in the two bars T_1 and T_2, prevents any motion of these about the axis of their rods. As shown by Fig. IV., an adjusting screw, passing through the bar, and a flat spring *t* on one side of the square perforation of the bar (T_1 or T_2), enforce steadiness of motion.

The upright pins *g g* (I.), which are tipped with sharp agate cones, arrest the end-bearings by rising into corresponding conical hollows in the latter. (Fig. 6, though taken from an Oertling balance, will give an idea of the way in which these pins work.) The two slanting lines O O (Fig. I.) are meant to indicate two supports, which pass through slots in the pillar S and the bronze rod F, and are fixed to the inner rod L, to lend additional rigidity and steadiness of motion to the end-bearings arrestment.

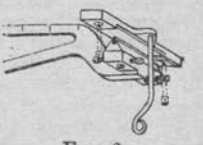


FIG. 6.

The arrestment of the beam is effected by two adjustable piers Z rising from the bar T_1 of the bronze rod. The tops of these piers carry roof-shaped agate bearings, in which the arrested beam lies with its lower (bevelled) edge. This would be sufficient to keep the beam from turning. To hinder it from moving progressively, there is a horizontal frame L (Figs. III. and IV.) united with bar T_1 by two little pillars G, G, and carrying two agate bearings, a roof-shaped one at the hinder end and a plane one at the front end of the middle (agate) knife. The roof-shaped bearing receives that end of the middle knife as the roof-shaped bearing of an ordinary balance would (so that by it, and the two beam-supports, three points of the arrested beam are fixed in prescribed positions); the plane bearing in front only supports the knife as it rises up to it on arresting. This plane bearing is adjustable by means of a screw, so that the arrested central knife-edge can be made rigorously parallel to the fixed central bearing of the working instrument.

There are three eccentrics, all attached to the same axis and governed by the same handle (Fig. II.), one, A, for the bronze rod F, a second, B, for the inner steel rod L, and a third, C, for a pan-arrestment, whose mode of acting will readily be seen by a glance at Fig. I. When the handle stands so that line *p* (Fig. I.) is vertical, the beam is arrested; after this point has been passed, the beam-supports remain at the same altitude, but, on turning the handle further, bar T_2 is raised to lift the terminal bearings as soon as line *q* stands vertical. The last third of the motion of the handle arrests the pans.

The principal feature in Messrs. Staudinger's Nachfolger's arrestment obviously is the relative independence of the beam-arrestment and of the end-bearings arrestment. In most other movable frame systems there is only one frame for both, and things are arranged so that the middle edge is held fast after the end-

bearings have been lifted by a hair's breadth, and that the upward motion comes to an end as soon as the middle knife is just visible above its bearing. A refinement upon this construction is to merely effect the three contacts, and then, by means of a special eccentric, to let the middle bearing drop through a distance of 0·1 or 0·2 mm.

Whilst all the several points of a rigid though movable arrestment-bar move up and down in vertical straight lines, the end-edges of the vibrating beam describe circular arcs. Hence whenever the bar is raised against the *slanting* beam, the end-bearings *tend* to slide over their knives and to spoil them. To preclude the possibility of this, Becker & Sons, in their finest balances, make the bar for the end bearings arrestment of two halves which are hinged on to the pillar in or very near the axis of rotation. Sartorius adopted this system and brought it into a slightly different form, regarding which we refer to Bibl. 4, where it is illustrated by a drawing.

In a balance which has only plane bearings, no kind of arrestment, of course, will give satisfaction, unless its several parts, and also the pillar and the sole, are sufficiently substantial to ensure absolute constancy of configuration and absolute steadiness of motion even after long-continued use. The old masters used to pay great attention to this important point, but it is sadly neglected by the majority of their present successors.

In a balance of which the end-pivots are self-adjusting, the movable arrestment frame assumes a very simple form. All that is needed is a small frame bearing V-shaped notches for arresting the middle knife in a prescribed position, and fixed to a horizontal bar with two projecting pins, in order, at the same time, to support the beam in a horizontal position. As these pins have no other function, the bar may be very light, and the whole system need not have that absolute steadiness of motion which is indispensable in the case of plane end-bearings.

The needle and scale serve to define the angular position of the beam. In all modern precision balances the needle points downwards, and is meant to embody a straight line passing through the axis of rotation and standing perpendicular on the line connecting the two point pivots A and B. The scale is attached to the pillar; its zero, if the stand is properly levelled, lies vertically below the axis of rotation. To enable the stand to be levelled, there must be either a plumb line or two spirit levels *fixed to the pillar*, and so adjusted that when they point to their zeros, the line connecting the zero of the scale with its projection on the middle edge is vertical. The scale should be so graduated that the needle-line, if produced, would cut, not the circle described by the needle's reference point, but the horizontal tangent to this circle, into pieces of equal length (*v. infra*). In most practical cases, however, this comes to the same as saying 'into pieces of equal angular value.' In balances provided with a fixed arrestment frame the scale should be made to move up and down with the beam, so that its position in reference to the needle remains constant. In most balances the end-point of the needle is just clear of the upper circular edge of the scale, but it is better to make its lowest portion almost linear, and let this project over the scale and almost touch it.

The rider.—Small weights are difficult to handle and easily lost. To avoid this inconvenience, Berzelius conceived the happy idea of dividing the right side of the beam, or rather the horizontal lever arm corresponding to it, into ten equal parts, and substituting one rider weighing ten centigrams for all the centigram and milligram pieces of the set of weights. Obviously the rider, when suspended at the first, second, &c. mark from the centre, acts like 1, 2, &c. centigrams placed in the pan, and it is equally obvious that every tenth of a division on the beam corresponds to one milligram of additional weight. This system was universally adopted and is still in use, only with this qualification, that we now apply it to the counting of the milligrams by means of a rider weighing ten milligrams. The reason for the change is obvious. In most balances the points 0 and 10 of the rider-scale are inaccessible. Becker & Sons avoid this inconvenience by dividing the arm into twelve parts, and supplying a rider weighing twelve milligrams. Other makers, for instance, Messrs. Verbeek & Peckholdt, of Dresden, make the top bar of their beams exactly horizontal, and, besides keeping it clear of impediments, make it project beyond the terminal edges. One of the advantages of this system is that, in the case of a short beam, it enables us to double the degrees of the rider scale, by dividing each arm into only five (integer) parts, numbering these from the left knife onwards and using a rider weighing five milligrams. Only, if we do so, the rider suspended at the zero must be counted part and parcel of the instrument. Bunge provides a special rider-bar so contrived that the path of the rider lies in the plane of the three axes. This, *theoretically*, is the most perfect arrangement.

A rider arrangement, to be complete, must be supplemented by a mechanical contrivance enabling one to shift the rider while the balance case is closed, and to do so with greater rapidity, ease, and certainty than would be afforded by a forceps, supposing the case to be open. Rider-guides fulfilling this latter condition are scarce; even with the best the rider drops down occasionally, and has to be searched for.

To avoid this source of annoyance Hempel does away with the rider and substitutes for it a vane with a limb graduated into milligrams (*v. infra*).

The gravity bob—a small button or disc of metal so attached to a wire standing vertically on the top of the beam exactly above the axis of rotation that it can be screwed up and down along the whole range of the wire. It enables one to raise or lower the centre of gravity of the beam, and thus to establish any desirable degree of sensibility.

A bob thus constructed meets all the requirements of the balance maker, but for the chemist who uses the balance it is desirable to have an arrangement which enables him at a moment's notice to establish any predetermined degree of sensibility. Such an arrangement was invented by the writer some years ago (Bibl. 8 and 5). It consists of a small bob fixed by mere friction to the upper end of the needle, which at that part has the form of a triangular prism, and is provided with a graduation. The mode of standardising the scale is explained below.

Some arrangement for establishing perfect equilibrium in the unloaded instrument is required. A small bob screwing along a horizontal wire fixed to some convenient part of the beam answers best. Less convenient is a 'vane,' meaning a little movable horizontal lever attached to the lowest point of the wire, which carries the ordinary gravity-bob, or to the upper part of the needle. To understand the working of the vane—and at the same time that of Hempel's invention above referred to—substitute for the vane an equivalent rigid line (Fig. 7). If the vane-line stands in the position

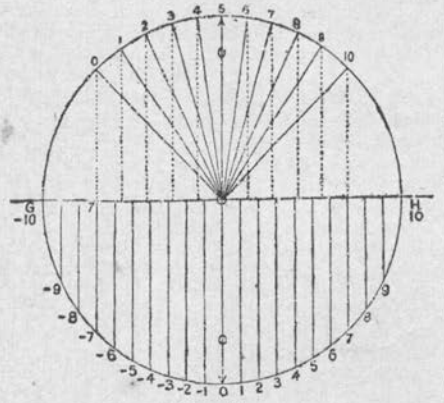


FIG. 7.

OO—*i.e.*, if it is parallel to the middle knife—it adds no weight to either side, if turned through 90° into position O (10), it virtually adds, let us say, 10 milligrams to the charge of the right pan. Divide the line O (10) into ten equal parts, erect an ordinate in each point, and you find the points 0, 1, 2, 3, &c., of the circular path of the end-point of the vane, to which the vane-line must point, if the virtual addition to the right pan is to be equal to 0, 1, 2....10 milligrams. A glance at the figure shows one weak point in the vane contrivance. There is, however, no need of our dividing the circular limb exactly in the way of our figure. We may, for instance, place the zero at the −7 and the ten at the +7 of our figure, divide the interval between the projections on line (10) ($\overline{10}$) of +7 and −7 into ten equal parts, and so adjust the mass of the vane and its distribution that, by turning it from the new zero (at −7) to the new '10' (at +7), we virtually add 10 milligrams to the right charge. The degrees, corresponding each to 1 milligram, then become so nearly equal to one another that the subdivision of each into ten parts of equal angular value is permissible.

THE THEORY OF THE BALANCE.

For a first approximation imagine a balance which is ideally perfect, and assume it to be charged with P grams from the left and with P grams from the right point pivot. The balance, when free to vibrate, can remain at rest in only its normal position, and if brought out of it will vibrate about it as a pendulum, because the two charges are equivalent statically to one heavy particle weighing 2P, situated in the central knife-edge. Now, put a small overweight Δ on, say, the right pan; the position of potential rest will shift, and the beam, to reach it, must turn (downwards on the right side) through a certain angle α, which depends only on Δ and on the weight W of the empty beam, which latter we may assume to be concentrated in its centre of gravity C, the force 2P being obviously out of consideration. But the two weights, Δ at *b* and W at C, are equivalent to a point weighing W+Δ and lying on the straight line *Cb* at a point C′, not far from C. The new position of rest is gained as soon as C′ lies vertically below the axis of rotation, or, to put it in other words, the right side of the beam goes down until the leverage of Δ is so far reduced and that of W has so far increased, that the two *momenta statica* are equal to each other.

Imagine now the axis of rotation were shifted vertically upwards through a small height *h*, but remained parallel to itself. The imaginary point weighing 2P now, as soon as the beam turns, *has* a lever and helps the weight W; the beam will turn through a less angle α' to gain its new position of rest, and, supposing 2P to increase, α' becomes less as 2P increases.

Imagine now the axis of rotation to be shifted downwards towards the centre of gravity. The heavy point weighing 2P grams now helps Δ, and the angle which separates the two positions of rest will become greater than the original angle; the greater 2P the greater will be the actual angle α''. But the two weights, W concentrated in C, and 2P concentrated in the centre of the line *ab*, taken jointly, are equivalent to one point C′ weighing W+2P grams, and situated on the straight line connecting the two points; and supposing 2P to increase gradually from *nil* onwards, C′, in the second case, will rise and rise, and at a certain value of 2P fall into the axis of rotation. The balance then has no definite position of rest; and if C′ rises still higher, the balance upsets. However small an overweight Δ may be put on either side, the beam would have to turn upside down to reach its one (theoretical) position of stable equilibrium.

The balance maker of course takes care so to adjust his instrument that even if the sensibility is at the highest value which the balance is meant to afford, and the two-sided charge 2P at its maximum likewise, the centre of gravity of the whole system lies on the safe side of the axis of rotation.

Assuming this condition to be fulfilled, the balance to be exactly equal armed and to be charged with a pan weighing p_0 grams and a load of p grams on each side, the angle α of deviation is governed by the equation

$$tg\alpha = \frac{\Delta l}{Ws + 2(p_0 + p)h}, \quad . \quad . \quad (1)$$

where l stands for the arm-length, s for the distance of the centre of gravity of the empty beam from the axis of rotation, and h for the distance of the axis of rotation from the plane of the two end-edges, the axis being assumed to lie *above* the plane. In the opposite case h must be assumed to be negative, or the *plus* sign before the second term in the denominator be replaced by a *minus* sign. But $tg\alpha$ is the ratio of the absolute length of scale (measured tangentially, *v. supra*) corresponding to angle α to

the distance l of the tangent-zero from the axis of rotation. Hence we have

$$n = \frac{\Delta l l}{Ws + 3(p_0 + p)h} = \Delta \cdot \text{'E'} \quad . \quad (2)$$

where, supposing I to be measured in tangential scale degrees, n may be read as meaning the number of degrees through which the needle turns in consequence of the addition of Δ. The product condensed into 'E' we will call the 'sensibility.'

The reciprocal of E, *i.e.* the number $E^{-1} = \frac{1}{E}$, is the weight-value of 1 degree of the scale —*i.e.* the particular Δ which makes $n = 1$. With a precision balance the milligram is a convenient unit for Δ.

For a balance provided with the writer's auxiliary bob, eq. (2) may conveniently be brought into the form

$$\frac{\Delta}{n} = E^{-1} = \frac{(Ws + 2Ph) + b(y_0 + y)}{ll} \quad . \quad (2a)$$

where b is the weight of the bob and y_0+y the distance of its centre of gravity from the axis of rotation y_0, being that distance which prevails when the bob is at its highest (zero) position. In a well-made balance the influence of P on E is small; we may therefore assume the P of the equation to be some average value, and, contracting constants, say, the weight-value of one degree is

$$E^{-1} = A + By \quad . \quad . \quad (3)$$

where A and B are constants; A obviously being that value which E^{-1} assumes when $y=0$. —B is easily determined by one trial at $y=$to its maximum, and the scale thus standardised.

The theory of the rider might be allowed to take care of itself if it were a general practice to place the rider's path exactly into the plane of the three axes. But such is not the case; this path, as a rule, lies above the plane, and each mark at its own altitude H. Let us therefore assume that, after the balance had been charged with P on each side, a rider weighing p had been suspended at a point of the beam corresponding to the fraction kl of the arm-length (at the $10k^{\text{th}}$ mark counting from the centre). If the beam stand horizontal, and a weight kp be placed in the opposite pan, the beam will remain in equilibrium, because we have $l(pk)=p(kl)$ whatever H may be; the rider where it is and the charge kp (virtually) in the left knife-edge are conjointly equivalent to a fixed point weighing $kp+p$, and situated on the straight line joining the left edge and the point $(10k)$ where the rider is. And this equivalence holds for the slanting beam as well, and is independent of P. But the sensibility of the beam with the rider on is evidently greater than it was with the rider off. Statically speaking, the weight of the beam and the two charges P and P are equivalent to a fixed point C_0 weighing $W'=W+2P$, and situated vertically below the axis of rotation at a distance S_0, and this particle, conjointly with the one embodied in the rider, is equivalent to a point weighing $W+2P+p$, and situated on the straight line between C_0 and the point where the rider sits. Referring to a system of rectangular co-ordinates whose X-axis passes through the centre of the central edge and is parallel to AB, and whose Y-axis passes through the same centre, we have for the position of the resultant point the equations

$$x(W' + p) = lkp \text{; and } y(W' + p) = W's_0 - pH$$

$$\therefore \frac{x}{y} = tg\alpha = kp\left\{\frac{l}{W's_0 - pH}\right\} \quad . \quad . \quad (4)$$

We see that if H be constant—*i.e.* if the rider-path be parallel to the plane of the three axes—$tg\alpha$ is proportional to the overweight kp virtually added to the charge of the right pan; but it is as well to notice that the $tg\alpha$ of our equation is different from the $(tg\alpha)_0$ which is brought about if, instead of hanging the rider on the $(10k)^{\text{th}}$ mark, we actually put kp units into the right pan. Obviously

$$(tg\alpha)_0 = (kp)\frac{l}{W's_0} \text{ and less than } tg\alpha \quad . \quad (5)$$

With a rider weighing only 10 milligrams, and, say, a hectogram balance, the term pH in the denominator comes to very little, but with a rider of ten times the weight it (as a rule) can no longer be neglected; such a rider cannot conveniently be used unless H is constant and the rider must always hang at the balance (at its zero, over, say, the central knife when it is not used as a weight), or else the sensibility has one value with the heavy rider on and another with the rider off. Another requisite is that notches cut into the beam be substituted for mere marks, and that the rider have a sharp edge to give sufficient constancy of position to its point of application.

From what we have said so far, it would appear that in a balance provided with a gravity-bob we can give the sensibility any value we may fancy. And so we can, but it does not follow that we can command any desired degree of *precision*. Because the three edges and bearings are not what they ought to be, and, as a little reflection shows, the effect of their defects is the same as if, say, the length of the right arm, instead of being at the constant value l, oscillated irregularly between $l-\lambda$ and $l+\lambda$, where λ is a very small length, which increases when W and P increase, but is independent of l. And this again is the same as if λ were *nil*, but the charge of, say, the right side, instead of being at a constant value P, varied irregularly from $P-\epsilon$ to $P+\epsilon$. In a given balance charged with a given P at each side ϵ is constant, but the corresponding angle of deviation β varies when the sensibility varies. Within this angle β the balance is, so to say, in a state of indifferent equilibrium. By going a little more deeply into the matter, we easily satisfy ourselves that, even allowing for the fact that we cannot substitute a longer for a shorter beam without increasing the beam-weight, ϵ will increase when l becomes less. In a balance meant to afford a certain degree of precision, we cannot allow the arm-length to fall below a certain (very uncertain) value l_0.

A glance at eq. (2) would show, if it were not clear without it, that, if the three axes lie in exactly the same plane—*i.e.* if $h=0$—the sensibility becomes independent of the charge, which is a great convenience. But h obviously cannot be equal to *nil* at all charges; hence in the case of the best instruments it is regulated so that it has a small negative value when only

the pans are suspended, and, by the unavoidable deflection of the beam, becomes *nil* at some suitably selected medium charge, so that, from this charge upwards, it has small positive values. That such a degree of precision cannot be attained by purely constructive methods goes without saying; indeed, any precision balance requires to be '*adjusted*' before it is fit to be used. For this purpose the value of the h corresponding to the medium charge and the ratio of the actual arm-lengths $l' : l''$ must be determined and the errors h and $\frac{l'}{l''}-1$ corrected.

For the direct geometric measurement of h special apparatus have been constructed, which, in their present form, we believe, afford a sufficient degree of precision; but the final test always is (or at least was until lately) at a suitable position of the bob, to determine the weight-value E^{-1} of one degree of deviation for a series of charges, say, $p=0$, 50, 100 grams, &c., up to the maximum charge which the balance is intended to measure; and to at least *virtually* calculate the corresponding values h by means of eq. (2). Whether h is positive or negative, is of course seen from the values E^{-1} without calculation. Supposing now h has a greater value than can be tolerated, one of the knives must be lowered or raised until at a certain medium charge the three edges are as exactly as possible in one plane. Most mechanicians provide adjusting screws for this purpose which enable one to work in a systematic manner. Some, however (for instance, Becker & Sons, following the example of Deleuil), prefer to fix all the knives definitely and to alter the *form of the beam itself* by means of the hammer. If the central edge has to be lowered, the lower bar of the beam is struck (on both sides); if it is to be raised, the upper bar is struck, until the correction is presumably almost but not quite completely effected. The values E^{-1} are then again determined, and if they are not sufficiently near one another, the hammering is renewed until the adjustment is perfect. In a similar manner (or by means of adjusting screws) the two arms are made equal to each other. The test here is very simple. The balance, after having been brought to the highest degree of sensibility which it will stand at the highest charge P, is charged with *exactly* P grams on each side. The longer arm goes down, and by determining the small overweight which must be added to the other side to establish equilibrium, we can easily determine the ratio $l' : l''$ numerically. All these adjustments are effected by the mechanician, and when once effected are final. Some mechanicians—for instance, the Beckers—fix even the centre of gravity, but this is a mistake. A balance, to be complete, *must* have a movable 'bob' to enable the operator to give the sensibility that value which suits him best. What degree of sensibility should we choose? Answer: In general, the lowest degree which suffices for the purpose in hand. Supposing, for instance, we can neglect the half-milligram, it is of no use to screw up the bob any higher than necessary for rendering the angle of deviation corresponding to 0·5 milligram conveniently visible and no more, because the less the sensibility, the greater the range of weights determinable by the method of vibration, the greater, as is easily shown from eq. (2), the relative independence of the sensibility from the charge, and last, not least, the less the time of vibration. The time of vibration can of course not be allowed to fall below a certain minimum, or else the centres of gravity of the charges will not be able to follow the oscillations of the beam with sufficient promptitude. But this clause, with larger balances wrought at high precision, usually takes care of itself. The exact relation in a balance between the time of vibration t (in seconds) and the sensibility E is given by equation:

$$t^2 = \frac{l}{Rl}\left\{kW + 2P\right\}\cdot E \quad . \quad (6)$$

where R is the length of the mathematical pendulum beating seconds at the place of observation, P the total charge on one side, and k a numerical factor, kWl^2 being the *momentum inertiæ* of the empty beam. With the customary perforated rhombus or triangle, k is very nearly equal to $\frac{1}{3}$. From the equation we clearly see that with a 'bob' of sufficient range we can choose our own time of vibration or our own sensibility, but we cannot choose both, in a ready-made balance. It stands differently with a *balance to be constructed*. To avoid indefiniteness, let us assume that we wished to design a balance for weighing quantities up to 100 grams with a toleration of 0·1 mgr. Let us assume also that we had made up our minds regarding the material and the general form for the beam, and that we had defined the latter so that the relation between arm-length l, and weight W, were in accordance with an equation of the form

$$W = C + Bl \quad . \quad . \quad . \quad (7)$$

where W includes the empty pans, C designates the conjoint weight of all that which is independent of l; and B stands for the weight of the rest if the arm-length $l=1$. Our equation now assumes this form

$$t^2 = \frac{l}{Rl}\left\{C^1 + 2p + bl\right\}E \quad . \quad . \quad (8)$$

where p stands for the charge in each pan. This equation affords some guidance in the selection of l. Assuming for E a value which renders the decimilligram just visible, and taking $p=0$, we substitute for t the smallest admissible value and solve our equation in regard to l. Of course cannot be allowed to fall below that minimum l_0 (*v. supra*) at which the inherent error would rise to anything like 0·1 mgr. Where does this limit value l_0 lie? Staudinger used to draw the line at 200, Oertling at 180 millimetres, and similar values were adopted by other makers, until Bunge, some twenty-five years ago, showed in the most direct manner possible that a sufficient degree of constancy can be attained with an arm-length of as little as 60 millimetres. Thanks to the general excellence of Bunge's work his short beams soon became very popular with chemists, and the fact that almost all other German makers have since come to adopt the Bunge system shows that the additional perfection in the pivots which the short beam undoubtedly demands is not so difficult to realise as an outsider might be inclined to think. *Assuming this difficulty to be overcome*, it cannot be denied that the short in opposition to the long beam does offer certain advantages. 1st. It is relatively light, and hence

the working of the arrestment is a less effort. 2nd. It is less liable to irregularities through one-sided elevation of temperature. Perhaps we may add that, 3rd, it is easier in its case than in that of the long beam to make a smooth-working arrestment, and on this account chiefly it enables one to weigh more quickly. 4th, and *least* in our opinion, it vibrates more quickly. Not that we value this last advantage at nothing. The writer's auxiliary bob indeed was invented with the very object of remedying the corresponding defect in the older form of the instrument, being originally intended to be used thus. In the outset, place the bob far down, say to the mark where 1° of deviation corresponds to 2 mgrs. or some other value securing great rapidity of vibration, and establish equilibrium as far as thus possible. Then raise the bob to the mark at which 1°=0·1 mgr., allow to vibrate, shift the rider correspondingly, and verify your result. The writer, however, soon came to find this method less convenient than he had expected, and adopted another very obvious expedient. It is easy in any beam to bring down the time of vibration to the least value one could reasonably wish for by screwing down the bob to the corresponding place. This, of course, may render the decimilligram invisible to the naked eye. But why not help the eye by optical means? An ordinary lens magnifying six times linearly affords more than there is any occasion for; only it magnifies the parallactic error as well, and the effort to avoid this error strains the eye very unpleasantly. This experience led the writer to the following combination, which he found to give perfect satisfaction. A narrow ivory scale divided into degrees of about 0·1 mm. is fixed slantingly to the needle pretty far down, yet far enough up for not obscuring the ordinary scale which does duty as usual; on the other hand, a compound microscope of feeble power, which passes through the central fixed portion of the front pane of the case, is fixed slantingly to the *pillar*. The microscope has one vertical 'wire' in its focus which acts as a needle. As the microscope inverts its images, the apparent motion of the wire in reference to the scale (which one easily persuades himself is fixed) is the same in sense as the real motion of the needle in reference to the ordinary scale, so that mistakes in regard to the + and − are avoided. The ordinary scale is graduated after the micro-scale so that each of its degrees is equal in angular value to 10° of the latter. The writer some five years ago caused Mr. Oertling to apply this arrangement to two of his balances, and he has found it to work very satisfactorily. Although it was originally intended chiefly for special occasions—the adjusting of weights, &c.—it is used even for our every-day work, as it was found that the microscope puts a less strain on the eye than the naked-eye reading of the ordinary scale. The microscopic arrangement described adds about 3*l.* to the cost of the balance. A cheaper arrangement is the following. A micro-scale, divided conveniently into fifth-millimetres, is fixed slantingly to the pillar, the needle at the corresponding part is shaped thus,

and a hair by means of capillary perforations is stretched out between *a* and *b*; the hair is parallel to the face of the scale, and only some 0·2 to 0·5 mm. removed from it. A short terrestrial telescope, fixed in the central (fixed) part of the front-pane of the case, serves for the readings. The object glass serves only to produce an image of the scale and hair within the tube, which the eye-piece (a compound microscope) magnifies as far as necessary. As the telescope need not be perfectly steady, it can be fixed at a relatively low cost. We have used this arrangement in connection with one of our balances for over two years, and found it to be almost as good as the one first described.

On the Setting up and Testing of a Precision Balance.

A real precision balance, to be able to do justice to itself, must stand on a very steady support, in a room where it is not exposed to one-sided changes of temperature. The light should fall in from the back of the observer. The best support, of course, is a pillar of masonry, standing directly on the earth. Next after it (in a substantially built building) comes a shelf fixed to the wall by strong brackets. A good heavy table, however, suffices in practice. In a large city the street traffic becomes very inconvenient in weighing. Its effect can be minimised by putting small pieces of thick vulcanised-rubber plate between the legs of the case and the table. In the examination of a newly set-up balance we naturally begin by seeing that the arrestment, the rider-shifting apparatus, &c., are in good order, we then level the case, and next leave the balance to itself for some four hours at least, to enable it to acquire the temperature of the room. After these preliminaries we proceed to the following determinations.

Determination of the inherent error ϵ.—For this purpose we charge the balance equally on both sides with the highest weight which it is intended to measure (a hectogram balance, for instance, with a hundred-gram piece on each side), and after having established approximate equilibrium at the highest degree of sensibility which the balance will stand at this charge without giving obviously inconstant readings, determine the exact position of rest, first with the two hectograms in the centres of their pans, and then, in a series of successive experiments, with one or other of the hectograms placed at some point of the edge of its pan so as to give any non-parallelism in the axes or any other defect in the terminal pivots a good chance of influencing the result, taking care to interpolate occasionally an experiment with the two weights centrally placed in order to see if the balance still gives the same readings as it did at first. If it does not, this is probably owing to external causes, such as unequal heating of the two arms. To be able to translate degrees of deviation into differences of weight, we must at some stage make two successive determinations of the position of rest, one with P′ in the left and P″ in the right pan (P′ and P″ stand for the two hectogram-pieces) and another with, say, one milligram added to P″. For the precise determination of a position of rest, we cause the balance to vibrate moderately, and (neglecting

the first reading as being in general liable to irregularities), record 3, 5, 7 . . . successive turning-points of the needle, applying a + to scale-points lying to the left, and a − to scale-points lying to the right of the zero (or *vice versâ*); an odd number in any case in order to correct for the retarding effect of the resistance of the air, &c.; those influences, in other words, through which the needle, supposing it to start from −4°, at the end of a double vibration, does not come back to exactly −4°, but perhaps to −3·7°. The algebraic sum of any two successive readings gives the point a of the scale at which the needle would come to rest, *in half-degrees*, and there is no reason why the half-degree should not be adopted as a convenient unit for the purpose in hand. Supposing the readings to be

	a_1	a_2	a_3	a_4	a_5
(Example)	+3·7	−2·7	+3·5	−2·4	+3·5

we have for a the values: $a_1+a_2=+1·0$; $a_2+a_3=+0·8$; $a_3+a_4=+1·1$; $a_4+a_5=+1·1$—Mean $=+1·0$.

The mean value of the four results is put down as *the* value of a. Supposing a, through the addition of Δ milligrams to the right charge to increase by n demi-degrees, then $E=\frac{n}{\Delta}(=2$ 'E' in the sense of our equation (2)) *is* the sensibility in demi-degrees; and its reciprocal $E^{-1}=\frac{\Delta}{n}\left(=\frac{1}{2E}\right.$ . . . of equation (2)$\left.\right)$ the weight-value of the demi-degree in milligrams. Supposing the values for a obtained with abnormal positions of the charges to be a_1, a_2, a_3, &c., instead of the mean value a_0, corresponding to the centrally placed charges, then $(a_0-a_1)E^{-1}=v_1$, $(a_0-a_2)E^{-1}=v_2$, &c., give each a value for the *inconstancy* of the balance in milligrams (or rather fractions of a milligram, it is to be hoped). According to a rule deduced from the law of frequency of error, the computation

$$r=\frac{0·845}{\sqrt{n(n-1)}}(v_1+v_2+v_3+\ .\ .\ .\ .\ .)$$

where all the v's must be taken as positive, gives the 'probable' weight-value of the deviation of any one a from a_0, meaning that value of $(a_0-a)E^{-1}$ which, in a *very large number* of determinations, is as often exceeded as not reached. But in practice the number of determinations made is never sufficiently great to bring out anything like a close approximation to the law, and it suffices to take r as being equal to 0·845 times the mean of all the values v, and adopt it as sufficiently near to the theoretical 'ϵ.' The probability that, in a given case, $(a_0-a)E^{-1}$ *exceeds*

	$2r$	$3r$	$4r$	$5r$
is	0·18	0·04	0·007	0·0007

respectively.

In these determinations, if the balance lacks a microscopic reading arrangement, it is as well to read from a distance with a telescope, to avoid the parallactic error which we have no right to charge against the balance.

Determination of h.—All that is necessary is to determine the weight value of one degree in the sense of equation (2) for, say, $p=100$, 75, 50, 25, 0 grams, and to calculate the corresponding values h. In a good balance h is so small that (supposing our rule regarding the adjustment of the bob to be followed) the sensibility remains almost constant from $p=0$ to $p=100$ grams. Hence, practically, it suffices to adjust the bob so that at a convenient average charge (where 'average' refers to the most frequently occurring values of p) one demi-degree corresponds to say $\frac{1}{2}$ or $\frac{1}{3}$ of a milligram *exactly*, and then to see what it is at other charges. If there is no sufficient constancy we enter the values E^{-1} found on a system of rectangular co-ordinates in function of the charges p, and draw the nearest curve to the points. This curve (if h were absolutely constant) would be a straight line. In any case it supplies the data for a table of values for E^{-1}. This table, however, must not be relied on in *standard* weighings, because the value h is subject to changes, for this reason amongst others, that the agate of the knives has a different coefficient of expansion from the metal of the beam.

The arm-lengths.—For the determination of the ratio of the arm-lengths, the orthodox method (for a hectogram balance) is to adjust two hectogram-pieces to exact equality, and, after having established equilibrium, to put one into the left and the other into the right pan, &c. But in practice the following method is better. Take any two fairly well adjusted hectograms and viewing them, one as a *standard* representing 100,000, the other as an *object* weighing x milligrams, go through the ordinary operation of weighing once with the object in the left pan and the standard in the right, and once the other way.

Supposing (using S as a symbol for 100,000 milligrams) we find

$$xl' = (S+\delta_1)l'' \ .\ .\ .\ .\ .\ \text{I}$$
$$xl'' = (S+\delta_2)l' \ .\ .\ .\ .\ .\ \text{II}$$

(where any δ may be negative), we have by division of I by II, and subsequent multiplication with $l'':l'$,

$$\left(\frac{l'}{l''}\right)^2=\frac{S+\delta'}{S+\delta_2}=\frac{1+\frac{\delta_1}{S}}{1+\frac{\delta_2}{S}}$$

whence, as a sufficient approximation,

$$\frac{l'}{l''}=1+\tfrac{1}{2}\left(\frac{\delta_1-\delta_2}{S}\right)$$

No maker who has a name to lose would care to send out a precision balance in which $1-\frac{l''}{l'}$ is more than $\pm 0·00005$ at the outside, although for any scientific purpose a considerably greater error could be tolerated. The corresponding adjustment indeed, while of the first importance in commercial balances, in precision balances is in a sense irrelevant.

Unequal-armed Lever Balances.

(1) *The steelyard or Roman balance.*—In it only the shorter arm (of the length l) bears a pan; the longer arm, by notches cut into its back, is divided into parts of equal length, l being the unit. The working points or lines of the notches should lie in the plane of the two edges, being so many bearings for the knife-edge forming part of a sliding weight adjusted to P units. The unloaded balance is in its position

of rest when the beam stands horizontal. To weigh a body, it is placed in the pan and the sliding weight shifted forwards from notch to notch until (when the weight hangs at the distance nl from the axis of rotation) the beam is again at rest in its horizontal position. We then have for the weight sought

$$xl = nl\mathrm{P} \text{ or } x = n\mathrm{P}.$$

As fully explained above, the principle of the steelyard is discounted in the modern precision balance for the determination of small differences of weight. In theory there is no objection to its extension to the determination of weights generally, but the technical difficulties to be overcome are great. On an equal-armed balance, whose beam is divided into 100 equal parts (from end to end), all weights from 0·0001 to 100 grams might be determined with three riders weighing half of (100, 1, and 0·01) gram respectively, but the realisation of 101 exact pivots is no small matter. Where relatively high precision is aimed at, it is better to provide only a small number of notches (say 10) and have a set of riders, weighing say 10, 1, 0·1, 0·01 grams respectively. The specific gravity balances of Westphal of Celle, are made on this principle. It strikes us that the steelyard principle might be discounted for the decimal subdivision of weights, thus:

Imagine a precision balance whose two arms measure $10l$ and $11l$ units. 10 grams placed in the pan of the longer arm are balanced by $10+1$ grams placed in that of the shorter; hence a 1-gram piece may be adjusted after two exact 10-gram pieces, &c.

The tangent balance has only *one* short arm, from which the pan is suspended; its centre of gravity lies low, so that the *momentum staticum* Ws of the beam assumes a high value, and even a considerable weight placed in the pan produces only a moderate angle of deviation. The needle moves along a circular limb divided so that the readings are proportional to the tangents of the respective angles of deviation, and give the corresponding weights directly. The equation $\Delta = \frac{tg\alpha \cdot Ws}{l}$ (*see* equation (1), above) holds theoretically for any value Δ, but the angular deviation corresponding to 1 gram of additional charge becomes less and less as the charge increases. The tangent balance, though useful for the rough weighing of letters, parcels, &c., is not available for exact gravimetric work.

Compound Lever Balances.

In all these, practical convenience and rapid working are gained at the expense of precision. In the *Roberval balance* the pans are above the system of levers (which as a rule is concealed in a box), so that there is room for bodies of even large dimensions. Our diagram, Fig. 8, is intended to explain only the *principle* of the machine, which in practice assumes an endless variety of forms.

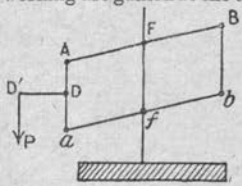


Fig. 8.

The beam consists of two parallel vertical parallelograms of which only the front one is represented in our figure. F and f (and F′ and f' in the other parallelogram) are fixed pivots, A, B, a and b (A′, B′, a', b', behind) are movable joints. On each side a horizontal bridge connects a point D on the vertical side Aa (and a similar point on Bb) with a corresponding point D′ on the back parallelogram (so that, for instance, Aa, $A'a'$, DD′ form one piece) and, from the centres of these bridges, vertical rods are arising which support the pans. Supposing each pan to be charged with P pounds, the centre of gravity of either of these two equal charges may lie in any of a great many positions about the respective pan, yet the statical effect is the same as if it were concentrated, one in the centre of the one bridge, and the other in the centre of the other; the two charges will balance each other, because, if the centre of gravity of one descends by h mm. that of the other rises by h mm., so that the work $\mathrm{P}h$ is the same on both sides. An over-weight added to one of the charges will bring down that side. The bars AB and A′B′ are relatively heavy beams, the lower bars ab and $a'b'$ are light. Hence it depends chiefly on the distribution of the mass in the beams AB and A′B′ whether the balance (if nearly equally charged) has a definite position of rest: but even if it has, it will never vibrate like an ordinary balance, on account of the great friction in the numerous pivots. If it could only be cured of this defect, the Roberval would be the ideal balance for the counter or ordinary weighings in the laboratory. This problem has been to some extent solved in the torsion balance of Springer, in which the axes are realised in stretched out horizontal bands of elastic steel, which act, so to say, as knives and bearings in one.

The '*torsion balance*' is made [1] in a great variety of forms, but the principle of construction is the same in all. The following description is

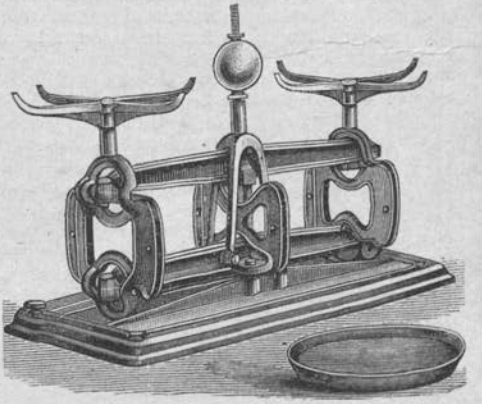


Fig. 9.

based upon the examination of what was sold as a high-class pair of counter-scales for loads up to 20 lbs. As shown by Fig. 9, the balance consists of two parallel beams united into a flexible parallelogram by means of three vertical frames, the bond of union in the case of each frame consisting of two horizontal bands of elastic steel,

[1] By the Torsion Balance and Scale Company, 92 Reade Street, New York.

which bridge over certain gaps of the frames, the middle portion of each band being firmly united with the respective beam end at its lower side by means of a screwed-on block of metal. In this instrument the beams measure 290 mm. from end pivot to end pivot, the steel bands are 5·6 mm. broad and 0·49 mm. thick; the length of the working part of a band is 58 mm., 29 on each side of the beam. The middle band lies below the plane of the two end bands by about 2 mm. The central frame, which does service as a pillar, is fixed to the sole of the instrument, the end frames are fixed only to their respective beam ends. Fig. 10, which is drawn to scale,

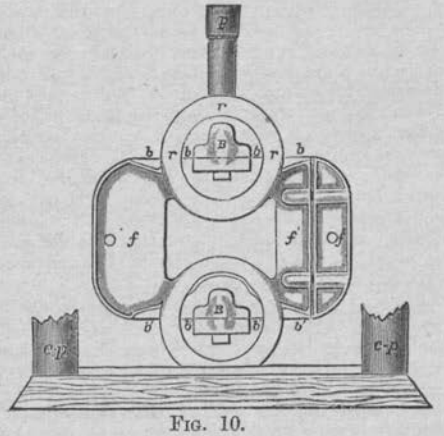


FIG. 10.

represents one of the end frames. The two steel bands of each frame, though independent of each other in their action, are really parts of one continuous band which is wound tightly round the edge of the frame, the ends meeting in B or B', where they are, we presume, riveted on. To give them the requisite degree of high tension, the frame, of which part of the right side is movable, is stretched laterally (by means of pegs fixed to the two sides of a vice and slipped through the two holes of the frame) and the gap which is thus produced between the two halves of the right side of the frame is made permanent by means of metal plates wedged into it. The central frame is somewhat differently shaped from the lateral ones; the upper ring, *r*, is omitted, to enable the upper beam to pass freely through between the legs of a stool fixed to the lower and terminating into a vertical peg which serves as a needle and carries a globular gravity bob. The bob, which in the case of the balance under consideration weighs 458 grams, *i.e.* more than a pound, can be raised or lowered to enable the sensibility of the instrument to be varied. The system of beams is inclosed within a case of plate-glass; the top plate supports an arch made of a metal tube from which an ivory scale graduated on both sides is suspended vertically so that its lower edge runs through a notch in the upper sharpened end of the needle to enable the vibrations to be read from either side.

To explain the working of the instrument, let us for a moment substitute for the steel bands so many linear wires, which, though unbendable, offer no resistance to torsional disfigurement. The torsion balance thus modified is in theory identical with the ideally perfect 'Roberval,' and, if the centres of gravity of the beams are in their axes of rotation, the parallelogram will be in a state of indifferent equilibrium at any shape which it may assume. To give it a definite position of rest, we must either shift (let us say one of) the centres of gravity vertically downwards, or else we must endow our ideal wires with torsional elasticity, which, of course, brings us back to the actual instrument. But the torsional elasticity of the steel bands is very considerably more than we want; its effect on the sensibility is the same as if (supposing the upper beam is suspended at its centre of gravity) that of the lower lay at a very considerable depth below its axis of rotation. To give the balance a sufficient degree of sensibility, we must raise the centre of gravity of say, the lower beam, until the stability of the position of rest is reduced to a sufficiently small value. In the actual instrument this is effected by means of the heavy gravity bob above referred to.

The principal advantage claimed for the torsion-balance, in contradistinction to the Roberval balance, is its freedom from friction; and this advantage it undoubtedly possesses, but it is compensated for to a large extent by the unavoidable viscosity in the elastic bands. The instrument described above, when equally charged on both sides, and with the bob sufficiently far down, vibrates like a precision balance of a high order; the position of rest as calculated from a series of couples of successive deviations of the needle, is remarkably constant up to at least a charge of 5 kilos. on each side; but once, when we determined the sensibility at first with no charge, then at a charge of 2 kilos., and lastly for a charge of 5 kilos., and then redetermined the sensibility of the unloaded instrument, we found that it was out of equilibrium to the extent of more than a decigram. We also found that the reading of the balance is not quite independent of the position of the loads on the pans.

The ordinary decimal balance, as used for weighing heavy loads, is a combination of levers as shown in Fig. 11. *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, are all joints or pivots; *a* and *h* rest on the fixed framework of the machine and consequently indirectly on the ground,

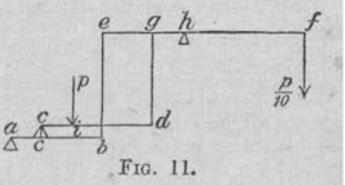


FIG. 11.

c rests on the lever *ab*. In the actual machine *cd* supports the bridge which accommodates the load, while a pan suspended at *f* receives the weights. The pan is so adjusted that it counterpoises the bridge. Suppose the load amounts to P units and its centre of gravity lies vertically above *i*; a portion P_c presses on the knife-edge at c and the rest $P_d = P - P_c$ pulls at *d* and with the same force at *g*. Now P_c pulling at *c* is equivalent to a less force ${}_bP_c$ pulling at *b*, and ${}_bP_c \cdot ab = P_c \cdot ac$, whence ${}_bP_c = P_c \frac{ac}{ab}$. But ${}_bP_c$ pulling at *b* or *e* is equivalent to a greater force ${}_gP_c$ pulling at *g* and ${}_gP_c \cdot gh = {}_bP_c \cdot eh$; hence ${}_gP_c = \frac{eh}{gh} \cdot {}_bP_c = \frac{eh}{gh} \cdot \frac{ac}{ab} \cdot P_c$.

The dimensions are so adjusted that $\frac{eh}{gh} = \frac{ab}{ac}$ whence $\frac{eh}{gh} \cdot \frac{ac}{ab} = 1$; hence the joint effect of P_c and P_d at g is the same as if they both, *i.e.* P, were suspended at g; and if, for instance, gh is $\frac{1}{10}$ of hf, $\frac{1}{10}$ P units in the pan will balance the P units lying on the bridge. In many balances of this kind the long arm hf is divided so that lesser weights can be determined by means of a rider.

Elasticity Balances.

Imagine an elastic solid body—beam, wire, spiral, &c.—to be held fast in one or more fixed points, and suppose some one other point a to be used as a pivot for the suspension of a load of P units. Point a will sink until, at a certain depth h, the strain developed by the deformation of the working body balances that weight P. As long as the working body is not stretched beyond its limit of perfect elasticity, the length h, if not proportional to, is at least a fixed function of P; hence the path of a can be graduated, at least empirically, so that each point of the scale corresponds to a fixed number of units of weight. This is the general principle of the multitude of *spring balances*. Sometimes a relatively strong spring is used to effect only a small displacement of a even with the highest charge, but this displacement is then multiplied by a system of levers, so that the least difference of weight which the balance is meant to show becomes visible. In a very neat kind of spring-balance, which has become popular, the displacement of a is, by means of levers and a toothed wheel, translated into the circular motion of a needle which moves along a divided circular limb like the hands of a clock on their dial.

Jolly constructed a *quasi*-precision spring-balance for sp.gr. determinations thus:—A long spiral of wire is suspended vertically in front of a vertical millimetre-scale, etched on a strip of plate glass which is silvered behind, so as to avoid the error of parallax. From the lower end of the spiral a light pan is suspended; the index is close above the pan at a convenient point. The instrument has never come into general use, because any second-class precision balance beats it in every sense. A similar remark applies to an ingenious little instrument invented by Ritchie for the determination of minute weights.

Ritchie's balance consists of a very light beam whose axis of rotation passes through its centre of gravity, and which is firmly united with a thin horizontal wire which lies in the axis of rotation. The hind end of the wire is absolutely fixed to the stand; the front end forms the continuation of the axis of a circular pin revolvable within a circular bearing. A needle fixed radially to the pin points to a divided circular limb. The empty balance is so arranged before use that the beam when horizontal is at rest. To determine a small weight (x mgr.), it is placed in, say, the right pan, and the wire turned from the right to the left by turning the pin until after the needle has passed through α degrees (where α may be more than 360°); the beam is again at rest when horizontal. We then have $x = \text{const.}\ \alpha$. The constant must be determined by experiments with known weights. Sartorius of Göttingen used to apply the Ritchie arrangement to his precision balances for the determination of differences of weight from 10 mgrs. downwards (Bibl. 5), but he has long since given up the notion: at any rate it is no longer to be seen in his price list. A Ritchie balance might perhaps do well for the adjusting of small weights, but a small precision steelyard would work infinitely better.

Sartorius' combination, if provided with a relatively strong wire, might make a handy instrument for the rapid (approximate) determination of weights without the use of any standard mass less than 1 gram.

The Hydrostatic Balance

is a hydrometer provided with a relatively large body and a narrow neck, and so adjusted that it weighs considerably less than its own volume of water. The top end of the neck bears a horizontal table, which serves as a pan, or, what is better, is provided with a horizontal system of cross-bars, from whose ends a pan is suspended by means of wires or chains, below the shelf supporting the vessel containing the floating hydrometer. A certain weight P, placed in the pan, brings down the hydrometer so far that the surface of the water touches a certain mark on the stem. If an unknown weight x requires to be supplemented by standard weights equal to p units, to produce the same effect, $x+p=P$, or $x=P-p$. Even for P= let us say 2 kilos., the neck need not be thicker than an ordinary knitting needle, so that the milligram, as a difference of weight, becomes perceptible. Wherever a precision balance has to be extemporised this instrument is useful; but it has no other *raison d'être*. Indeed of all the multitude of machines which the science of mechanics places at our disposal for the measurement of weights, the equal-armed lever-pendulum is the only one which, so far, has worked satisfactorily for precise gravimetric determinations.

A balance based on dynamical principles has been proposed. Imagine a pendulum provided with a shiftable bob above the fulcrum, and carrying a pan attached to the bottom end of the rod by a hook-and-eye. In a given instrument the time of vibration is a function of the distance of the bob from the fulcrum, and of the weight x of the object in the pan, and consequently the weight x is a function of the other variables.

Bibliography.—(1) *Leonhard Euler*: First Development of the Theory of the Balance; Trans. of the Petersburg Academy.

(2) *Wilhelm Weber*: Balance: Göttingen gelehrte Anzeigen for 1837, 287. Description and Drawing in Carl's Reportorium für physikalische Technik, 1, 18.

(3) *Löwenherz*: Report on Metrological Instruments in Bericht uber die wissenschaftlichen Apparate auf der Londoner Ausstellung in 1876; Braunschweig, 1881. Vacuum Balances, 223–232. Balance Beams, 232–237. The Pivots: Modes of Fixing the Knives, 237–245; Bearings, 246–247; Arrestments, 248–253.

(4) *Löwenherz*: Zeitschrift fur Instrumentenkunde for 1881, 125; Report on Sartorius' Hinged Arrestment Frame.

(5) *Löwenherz*; same Journal, year 1881, 184. A Report on Apparatus for Measuring

Small Weights by the Torsion of Wires: Hooke, Ritchie, Sartorius. Full drawing of Sartorius' contrivance on p. 188.

(6) *Dittmar*; Waage des Chemikers; same Journal, year 1881, 313–326.

(7) *Dittmar*; same Journal, year 1882, 63; Mikroscopische Ablesungsvorrichtung für feine Waagen.

(8) *Dittmar*; R. Soc. Ed. Proc. for 1876; Chem. News, 33, 157. W. D.

BALANOPHONE WAX *v.* WAXES.

BALATA is the product obtained by coagulating the latex of *Mimusops globosa*, Gaertn., a large forest tree, belonging to the natural order Sapotaceæ, which is a native of British, Dutch, and French Guiana, Venezuela, Trinidad, Jamaica, and probably Brazil north of the Amazon. In British Guiana and the West Indies the tree is known as the 'bullet' or 'bully' tree.

In physical properties and chemical composition, balata resembles true guttapercha, for which it is the best natural substitute, and it is of interest in this connection that the tree yielding it belongs to the same order as the trees (*Palaquium* spp.) which furnish guttapercha.

The balata trees are tapped by making a series of incisions in the bark, so arranged that the latex can run down to the base of the trunk, where it is collected in a calabash. The latex is afterwards poured into shallow wooden vessels, which are usually greased or rubbed with soap to prevent the balata from adhering to them, and allowed to stand exposed to the air until it has coagulated spontaneously; a sheet of balata is thus formed, which, when sufficiently hard, is removed from the vessel and hung up to dry. The coagulation of the latex may also be brought about by boiling, in which case the balata is obtained in the form of 'block.' Formerly it was the custom to fell the trees and then to cut rings in the bark in order to obtain the latex, but this practice, which involves the destruction of the trees, is now prevented as far as possible.

The latex of balata trees usually flows freely, and, in favourable circumstances, the yield from a tree 15–20 inches in diameter, tapped to a height of 8 feet, is about 3 pints, representing from 1½ to 2 lb. of dry balata.

Commercial balata may be either grey, pinkish or brown. When immersed in hot water it behaves like guttapercha, becoming soft and plastic, and, on cooling, it slowly hardens again without becoming brittle.

Balata is also similar to guttapercha (*q.v.*) in chemical composition, consisting essentially of a hydrocarbon (*gutta*), of empirical formula $C_{10}H_{16}$, associated with resins; the commercial product also includes varying amounts of insoluble matter (dirt) and moisture. Balata contains a much higher proportion of resins than good guttapercha, and is therefore inferior in quality to the latter; when compared with guttapercha containing a similar amount of resin, it is found to be a little softer and more flexible.

The composition of balata is shown by the following typical analyses:—

Description.	Source.	Moisture per cent.	Gutta per cent.	Resin per cent.	Proteid per cent.	Dirt per cent.	Ash per cent.
Specially prepared sheet [1]	British Guiana	1·9	49·7	44·0	3·8	nil	0·6
Block balata [1] . .	Venezuela	1·8	45·7	44·2	3·0	5·3	[1·28]
Commercial specimens [2 3]	Mostly British Guiana	13·8	41·5	34·8	—	9·9	—
Balata [2]	Dutch Guiana	5·3	43·5	36·9	—	14·3	—

The gutta of balata is very tenacious and of excellent quality; it is insoluble in alcohol, acetone, ether, or cold petroleum spirit, but is readily dissolved by chloroform, carbon disulphide, or boiling petroleum spirit. The resins present are similar to those of guttapercha, and consist of (1) a white crystalline resin (*albane*) soluble in hot but insoluble in cold alcohol; and (2) an amorphous yellow resin (*fluavile*) soluble in cold alcohol. An examination of the total resin of balata by Obach showed that it consisted of about 2 parts of albane to 3 parts of fluavile.

Balata is utilised commercially as a substitute for guttapercha. Its chief applications are for the manufacture of belting, in which the balata is interposed between layers of canvas; for insulating purposes; and for the manufacture of the covers of golf balls, after the removal of the greater part of the resin by solvents. It is also employed to a considerable extent for mixing with rubber, and for numerous minor purposes.

The bulk of the commercial supplies of balata are obtained from British and Dutch Guiana and Venezuela. H. B.

[1] Analysed at Imperial Institute.
[2] Analysed by Dr. Obach.
[3] Average figures for nineteen commercial lots representing 50 tons.

BALLISTITE *v.* EXPLOSIVES.

BALLOON or **FLEXIBLE VARNISH** *v.* VARNISH.

BALL SODA *v.* SODA MANUFACTURE, art. *Sodium*.

BALM OF COPAIBA *v.* OLEO-RESINS.

BALM OF GILEAD, *Mecca* or *Opobalsam* (*v.* OLEO-RESINS).

BALSAMS. The exudations of plants, whether spontaneous or promoted by incisions made in their stems or roots, consist chiefly of resin, gum, volatile oil, and certain aromatic acids, or mixtures of these. The *resins* are characterised by insolubility in water and solubility in alcohol, the *gums* by solubility in water and insolubility in alcohol, and both by not being volatile without decomposition. *Volatile oils* may be distilled unchanged, and are solvents of resins. They are not obtained by the method of exudation except when they hold large quantities of resin in solution, giving rise to the important class of *oleo-resins*—such, for instance, as the so-called Canada balsam. Gum arabic is a familiar instance of a gum obtained direct from the plant;

mastic is an instance of a resin. The class of *gum-resins* may be represented by myrrh.

Now, amongst these resins and oleo-resins there is a group the members of which are marked by possessing a peculiar fragrant odour and agreeable pungent taste, which is due to the presence of free or combined cinnamic or benzoic acid. These are the *balsams*, and it is convenient to consider them as a class by themselves. The word 'balsam,' it is true, has sometimes been used in a wider sense—indeed, it was originally employed for an oleo-resin resembling the so-called Canada balsam; but it is more convenient to restrict the term to resins or oleo-resins which contain cinnamic or benzoic acid. The balsams have long been familiar to writers on materia medica, some of them being known to Pliny, and even earlier to the Greek physicians. They are favourite constituents of the incense used in the Greek and Roman churches, and while they cannot be said to have an important therapeutic value, they are reputed mild tonics and stimulants and are a common flavouring agent in expectorant medicines. The following are the more important:—

Benzoïn. *Gum Benjamin*; *Benzoïnum.* (*Benzoin*, Fr.; *Benzoëharz*, Ger.) The benzoïn of Java and Sumatra is derived from the thick-stemmed trees of *Styrax Benzoïn* (Dryander, Phil. Trans. 1787, 303; Bentl. a. Trim. 169), while the more highly prized Siam benzoïn is probably obtained, according to Royle, from the *Styrax Finlaysoniana* (Wall). The source of Siam benzoïn is, however, still uncertain (Holmes, Pharm. J. [3] 14, 354). The first European writer to mention benzoïn is Batuta, who travelled in the East early in the fourteenth century, and from that time to the present day the drug has been an established article of materia medica. It is largely used for incense and in the preparation of fumigating pastilles, and enters into the well-known Friar's Balsam or compound tincture of benzoïn, a favourite dressing for wounds.

The juice exudes from the trees as the result of incisions, and it is allowed to harden before it is removed. During the first three years of the life of a tree the balsam dries in the form of *tears*. This is called *head* benzoïn, and is the most highly reputed. A less esteemed variety is obtained during the following seven or eight years, which is browner in colour and is called *belly* benzoïn. Lastly, the trees are split, and the commoner *foot* benzoïn is scraped off (*cf.* Flück. a. Hanb. 405).

Benzoïn consists essentially of a mixture of resins together with uncombined benzoic and sometimes cinnamic acids. The resins are entirely soluble in solution of potash and in alcohol, but by their behaviour toward other solvents they have been distinguished as *α-resin*, *β-resin*, &c. (Unverdorben, Pogg. Ann. 8, 397; Kopp, Compt. rend. 19, 1269; Van der Vliet, Annalen, 34, 177). The yield of *benzoic acid* varies from 12 to 20 p.c., being on an average about 14 p.c. Two methods are adopted for its extraction. By the first the benzoïn is mixed with sand and heated in a suitable vessel, over which is placed a paper or other receiver to collect the vapours of benzoic acid, which condense in beautiful tufts of acicular crystals. The second method consists in boiling the benzoïn with milk of lime, filtering, and after concentration of the calcium benzoate solution thus obtained, precipitating the benzoic acid by hydrochloric acid. Lüdy (Arch. Pharm. 231, 43) has shown that the *α-*, *β-*, and *γ-* resins of the earlier investigators are mixtures of the partially hydrolysed cinnamates of the resin alcohols present, the *α*-resin being the least and the *γ-* the most hydrolysed. He also finds that benzoïn from Sumatra contains *benzoic acid*, *cinnamene*, traces of *benzaldehyde* and *benzene*, 1 p.c. of *vanillin*, 1 p.c. of *phenylpropyl cinnamate*, 2–3 p.c. of *cinnamyl cinnamate*, and a mixture of a little *benzoresinol cinnamate* with much *resinotannol cinnamate*, this mixture forming the main constituent of the balsam. In addition, woody impurities occur to the extent of 14–17 p.c., also free *cinnamic acid*, but to a less extent than free benzoic acid. By hydrolysis of the mixture of benzoresinol and resinotannol cinnamates the two alcohols are obtained, *benzoresinol* $C_{16}H_{26}O_2$, consisting of white crystals, and *resinotannol* $C_{18}H_{20}O_4$, a brown amorphous powder.

Siamese benzoïn also examined by Lüdy (Arch. Pharm. 231, 461) differs from Sumatra benzoïn by containing no cinnamic acid either free or combined, the main constituent being a mixture of a little benzoresinol benzoate with much *siaresinotannol benzoate*. The alcohols obtained by the hydrolysis of the resin are present in the proportion of about 1 : 11. The benzoresinol is identical with that obtained from Sumatra benzoïn and crystallises in white prisms; m.p. 272°. *Siaresinotannol* $C_{12}H_{14}O_3$ is a brown powder very similar to resinotannol obtained from benzoïn of Sumatra.

Benzoïn, with the exception of woody fragments always present in the cake variety, should dissolve in five times its weight of alcohol, and this solution should give with water a milky emulsion having an acid reaction. When benzoïn is boiled with milk of lime, the hot filtrate should not give off the odour of oil of bitter almonds on the addition of a solution of potassium permanganate. This latter test guards against the addition of cinnamic acid (*cf.* U.S. and Ger. Pharm.).

Peru. *Balsamum Peruvianum.* (*Baume de Pérou*, Fr.; *Perubalsam*, Ger.)

A dark molasses-like liquid obtained in the State of Salvador in Central America from trees of *Myroxylon Pereira* (Klotzsch). Description, *v.* Bentl. a. Trim. 83. Balsam of Peru was probably introduced into Europe soon after the Spanish conquest of Guatemala in 1524 (Flück. a. Hanb. 206). The bark is bruised and scorched late in the autumn, and the exudation excited by this means is collected (Flück. a. Hanb. 207; Dorat, Amer. J. Pharm. [3] 8, 302; Hanbury, Pharm. J. [3] 5, 241, 315).

Balsam of Peru sinks in water, in which it is insoluble. It has a sp. gr. of 1·135 to 1·150. It is soluble in absolute alcohol, chloroform, acetone, and glacial acetic acid. Examined by Kraut (Annalen, 152, 129) and Kachler (Ber. 2, 512), the chief constituent of Peru balsam was supposed to be *cinnameïn*, benzyl cinnamate $C_6H_5{\cdot}CH:CH{\cdot}COOC_7H_7$. Kachler's analysis of Peru balsam is:—cinnamic acid 46 p.c., benzyl alcohol 20 p.c., resin 32 p.c. *Cf.* Attfield (J. 1863, 557); Delafontaine (Z. 1869, 156) finds in addition to benzyl cinnamate, *cinnamyl*

cinnamate or *styracin*. Trog (Arch. Pharm. 232, 70) by suitable treatment has divided Peru balsam into two constituents, an oil and a resin. The liquid portion known as cinnamein to the earlier investigators consists of benzyl benzoate with a small quantity of benzyl cinnamate; cinnamic acid and vanillin are found to be present in very small proportions. The resin when hydrolysed yields cinnamic acid and a small proportion of benzoic acid and *peruresinotannol*, a resin alcohol of the formula $C_{18}H_{20}O_5$. The balsam has also been examined by Thoms (Arch. Pharm. 237, 271).

Balsam of Peru has been much adulterated. Alcohol, fixed oils, copaiba, Canada turpentine, colophony, &c., have been used for this purpose. To ascertain its purity many methods have been devised. The specific gravity is important; this at once indicates alcohol if present. Alcohol may also be washed out by water and the reduction in volume noted. The U.S. Pharm. directs 10 drops of the balsam to be triturated with 20 drops of sulphuric acid, when a tough homogeneous cherry-red mixture should result. If this be washed after a few minutes with cold water it should be converted into a resinous mass, which is brittle when cold. This test indicates the absence of fixed oils and oleoresins. (For other modes of testing, *v.* Hirschsohn (Pharm. Zeit. 16, 81); Flückiger (Pharm. J. [3] 12, 45); Schlickum (Arch. Pharm. [3] 20, 498); MacEwan (Pharm. J. [3] 15, 236); Andrée (Arch. Pharm. [3] 22, 561); Denner (J. Pharm. Chim. [5] 18, 259). Testing of balsams, resins, and gum-resins: Pharm. J. [3] 17, 547.)

A *White Peru Balsam* is sometimes prepared in Salvador by expression from the fruit of the *Myroxylon Pereira*. It is a golden yellow semi-fluid granular crystalline mass containing a crystalline resin, *myroxocarpin* $C_{24}H_{24}O_3$, together with *styrolene*, *styracin*, and *cinnamic acid* (Stenhouse, Annalen, 77, 306; Pereira, Annalen, 77, 309; Scharling, Annalen, 97, 70; Harrison a. Malsch, J. 1875, 856). (For more recent investigations, *see* Germann (Arch. Pharm. 234, 641); Biltz (Chem. Zeit. 26, 436); Thoms a. Biltz (Chem. Zentr. 1904, ii. 1047); Hellström (Arch. Pharm. 243, 218). For other varieties of Peru balsam, *v.* Flück. a. Hanb. 210.)

Storax. *Liquid Storax*; *Balsamum Styracis*. (*Styrax Liquide*, Fr.; *Flüssiger Storax*, Ger.)

Storax balsam is derived from trees of *Liquidambar orientalis* (Miller), which are natives of Asia Minor (*cf.* Bentl. a. Trim. 107). This liquid storax is nearly related to another harder resin—the exudation of the *Styrax officinale* (Linn.). Both have been known since the later Greek period, but the latter is now no longer an article of commerce. To obtain the storax the outer bark of the tree is removed, and the inner bark is collected and boiled in water. The balsam melts and rises to the surface and is skimmed off.

Liquid storax is heavier than water, about the consistence of honey, and of a greyish-brown colour. It always contains a little water, which imparts to it a greyish opacity. When this is removed, by long standing or by heat, the resin becomes quite transparent. Dried in this way it is soluble in alcohol, ether, carbon disulphide, and volatile oils; but not in light petroleum. The odour of storax is agreeably balsamic and the taste aromatic and pungent. Examined with a microscope crystals may be detected which have been identified, the feathery spicular crystals as styracin, and the rectangular tables and short prisms as cinnamic acid.

Storax contains 10 p.c. to 20 p.c. of water, 13 p.c. to 18 p.c. of woody and inorganic impurities, leaving 56 p.c. to 72 p.c. of matter soluble in alcohol, which consists chiefly of styrolene, metastyrolene, cinnamic acid, styracin, and a large proportion of resin (Flück. a. Hanb. 275).

Styrolene or phenylethylene $C_6H_5{\cdot}CH{:}CH_2$ is obtained as a colourless mobile liquid by distilling storax with water (Bonastre, J. Pharm. Chim. 16, 88; Simon, Annalen, 31, 267). The solid polymeride of styrolene, *metastyrolene*, is also said to exist in storax. *Cinnamic acid* to the extent of 6 p.c. to 12 p.c. is obtained by boiling the balsam with sodium carbonate solution, which extracts it as a sodium salt from which the free acid is liberated by mineral acids.

Styracin or *cinnamyl cinnamate*

$$C_6H_5{\cdot}CH:CH{\cdot}COOC_9H_9$$

was originally discovered in storax by Bonastre. It may be obtained, after removal of the styrolene and cinnamic acid by treatment of the residue with ether, alcohol, or light petroleum in the form of a liquid, which with difficulty assumes a solid crystalline form, the crystals melting at 44° (Simon, Annalen, 31, 273; Toel, Annalen, 70, 1; Miller, Annalen, 188, 200). Styracin is readily converted by alkali into styrone or cinnamyl alcohol and cinnamate. *Benzyl alcohol* has been detected as a constituent of storax by Laubenheimer (Annalen, 164, 289). A good bibliography will be found in W. von Miller's memoir on the Chemical Compounds contained in Liquid Storax (Annalen, 188, 184), in which the author describes as present, in addition to the constituents already mentioned, *phenylpropyl cinnamate*, *ethyl cinnamate*, *ethyl vanillin*, large quantities of two alcoholic compounds, *α-* and *β-storesin*, and their cinnamic esters, a *sodium compound of storesin* and a *resin*. According to v. Itallie (Chem. Zentr. 1901, ii. 856), a good specimen of storax contains about 2·4 p.c. of substances insoluble in ether, 23·1 p.c. of free cinnamic acid, 14 p.c. of water, 22·5 p.c. of aromatic esters, 2 p.c. of styrene and vanillin, and 36 p.c. of resin. The total proportion of cinnamic acid is about 43 p.c.; the combined acid occurring partly in the resin and partly in the aromatic esters.

Storax is sometimes adulterated with turpentine. To detect this Hager dissolves the balsam in a little warm alcohol, and shakes this solution with light petroleum. The light petroleum on evaporation leaves a residue in which the terebinthinous odour is concentrated, and may be readily detected. Further, the residue so obtained, in the case of genuine storax, is colourless with a bluish opalescence, and represents 45–55 p.c. of the original balsam; but if turpentine be present the percentage is larger, and the residue has a yellowish colour (Ph. Centh. 15, 163).

Closely allied to liquid storax are the exudations from the *Styrax officinale* (Linn.), *Liquidambar styraciflua* (Linn.), a native of North America, the balsam of which was examined by Flückiger and v. Miller (Arch. Pharm. [3] 20, 646 a. 648). It is obtained in the

form of a sticky grey mass containing white crystalline portions mixed with fragments of wood and bark. Its composition does not differ essentially from that of Asiatic Storax (*v.* Itallie). *Liquidambar formosana* (Hance); and *Altingia excelsa* (Noronha) (*cf.* Flück. a. Hanb. 276; Tschirch a. v. Itallie, Arch. Pharm. 239, 541).

Tolu. *Balsamum tolutanum.* (*Baume de tolu*, Fr.; *Tolubalsam*, Ger.)

Monardes, in his book published in 1574, describing the products of the West Indies, is the first to mention balsam of tolu. Soon afterwards it was introduced into England. Tolu is the product of the trees of *Myroxylon Toluifera* (H. B. a. K.), natives of Venezuela and New Granada, and probably also of Ecuador and Brazil. (For botanical characters, *v.* Bentl. a. Trim. 84.) V-shaped incisions are made, and the concreted juice from time to time collected. This draining of the trees goes on for eight months of the year (Weir, Journ. R. Hort. Soc., May, 1864).

Balsam of tolu is a viscid resin, which on exposure hardens to a vitreous mass. It has an agreeable odour suggestive of vanilla, and has a decided aromatic taste. Crystals of cinnamic acid may be seen in tolu when thin layers are examined. It is soluble in alcohol, glacial acetic acid, acetone and chloroform, also in caustic potash. In benzene it is insoluble, and nearly so in carbon disulphide, volatile oils, and ether. Balsam of tolu consists for the most part of an *amorphous resin* similar to that left by carbon disulphide in the case of Peru balsam. This resin on hydrolysis yields *toluresinotannol* $C_{17}H_{18}O_5$, a lower homologue of peruresinotannol, a dark brown powder decomposing at 100° without melting. It gives colour reactions with ferric chloride and potassium dichromate, and precipitates with lead acetate and gelatin (Oberländer, Arch. Pharm. 232, 559). Treatment with water extracts from balsam of tolu *cinnamic acid* (Carles, J. Pharm. Chim. 19, 112), and according to Busse (Ber. 9, 830) it contains also *benzoic acid*, and both *benzyl benzoate* and *cinnamate*. Distilled with water, small quantities of a peculiar hydrocarbon pass over which has been called *tolene*. The yield, according to Deville, is 2 p.c. (Ann. Chim. Phys. [3] 3, 152). Tolene has the formula $C_{10}H_{16}$. Its sp. gr. at 10° is 0·858 (Kopp), and it boils at 170°, according to Deville and Scharling, or at 154°–160° (Kopp). Deville found tolene to have a vapour density of 5·1. This hydrocarbon does not appear to have been further studied or to be known in any other chemical relation.

Turpentine present as an adulteration in tolu may be detected by treatment with carbon disulphide, which has scarcely any solvent action on the genuine balsam; or by sulphuric acid, which imparts to tolu a cherry-red colour, whereas when turpentine is present the mixture turns black. A specimen of spurious tolu examined by Naylor was completely soluble in carbon disulphide (Pharm. J. [3] 8, 624). To test for added colophony, the sample is agitated with 4 to 5 times its weight of light petroleum and the filtrate shaken with its own volume of copper acetate solution (1 : 1000) when no green colour should be seen in the petroleum layer (Hirschsohn, Chem. Zentr. 1895, ii. 694).

Xanthorrhœa Balsams. A number of balsamic resins are obtained from the xanthorrhœas or grass trees of Australia. Seven species of these, the *arborea*, *australis*, *Hastile*, *media*, *minor*, *bracteata*, and *Pumilio* were described as early as 1810 by Brown (Prodromus Novæ Hollandiæ). The first two are arborescent trees, the third and fourth have short stems, and the last three are stemless. Hirschsohn (Pharm. Zeit. 16, 81) distinguishes three xanthorrhœa balsamic exudates; but of these only two are important, the *yellow* or *acaroid balsam* and the *red balsam* (Pereira, Mat. Med. 3rd ed. 1099).

Acaroid Balsam, Acaroid Resin, Resina Acaroides, Resin of Botany Bay. This balsam was first mentioned by Governor Phillips in 1789 (Voyage to Botany Bay). It exudes spontaneously from the *Xanthorrhœa Hastile* and, according to some writers, from the *X. arborea*. It has a yellow colour resembling gamboge, but sometimes has a deep red tint, and when heated evolves a balsamic odour. It is used in the preparation of sealing-wax and lacquers and japanner's gold-size. Among those who have investigated acaroid balsam are Lichtenstein (Crell's Ann. 2, 242); Schrader (Trommsdorff's Ann. 5, 96); Laugier (Ann. Chim. Phys. 76, 265); Widmann (Buchner's Repert. 22, 198); and Stenhouse (C. S. Mem. 3, 10; Annalen, 57, 84). Its chief constituents are *resin*, a trace of *volatile oil*, and *cinnamic*, *benzoic*, and *para-coumaric acids*, also *para-hydroxybenzaldehyde* and probably vanillin (Bamberger, Monatsh. 14, 633). The resin consists of *xanthoresinotannol* $C_{43}H_{44}O_{10}$, chiefly in form of *para-coumarate* (Hildebrand, (Arch. Pharm, 234, 698). (For properties of xanthorrhœa resin oil, *see* Schimmel and Co. (Chem. Zentr. 1898, i. 258); Haensel (Chem. Zeit, 1908, i. 1837).) By distilling acaroid balsam, Stenhouse obtained a light neutral oil containing *benzene* and *cinnamene*, and by treatment with nitric acid the same observer finds acaroid balsam to give so large a yield of *picric acid* that he recommends it as a convenient source of that compound. As much as 13 p.c. of *parahydroxybenzoic acid* is formed when acaroid balsam is fused with potash. Amongst the other products of this reaction, are *resorcinol*, *pyrocatechol*, and a *double compound of para-hydroxybenzoic and protocatechuic acids* $C_{14}H_{12}O_7,2H_2O$, which has been likewise obtained from benzoïn (Hlasiwetz and Barth, J. 1866, 630).

Red Balsam of Xanthorrhœa. Black-boy Gum. A red balsamic resin resembling dragon's blood. When heated it evolves a balsamic odour. This resin does not contain cinnamic or benzoic acid, it contains a small quantity of *para-hydroxybenzaldehyde*, and consists mainly of *erythroresinotannol* $C_{40}H_{40}O_{10}$, chiefly as *para*-coumarate (Bamberger, Hildebrand). A. S.

BAMBARA FAT *v.* BASSIA OILS.

BAMBOO. The ash of the shoots of these grasses (*Bambusa arundinacea* (Willd), *Gigantochloa verticillata* (Munro), &c.) contains from 30 to 40 p.c. of potash (K_2O), and constitutes a good source of potash. The fibres of the shoots supply an excellent paper-making material, and have been used for this purpose by the Chinese from time immemorial (Romanis, Chem. News, 45, 158; 46, 51; Nature 18, 50).

BAMBOOI FAT or **BAMBUK BUTTER** *v.* BASSIA OILS.

BANANA. The fruit of *Musa sapientium*, a plant growing freely in tropical countries. When ripe the pulp is rich in sucrose and invert sugar, but in the unripe condition contains much starch, and is extensively used for the preparation of banana flour in the Indian Archipelago, Brazil, the west coast of Africa, and the Pacific Islands.

Analyses by Leuscher (Zeitsch. öffentl. Chem. 1902, 8, 125) of (1) green husks, (2) ripe husks, (3) unripe fruit (pulp), (4) ripe fruit (pulp), and (5) banana-meal, are as follows:—

	(1)	(2)	(3)	(4)	(5)
Water . .	70·0	70·0	70·5	67·1	15·0
Crude protein .	2·0	2·9	3·9	5·0	7·0
Crude fat . .	4·5	4·1	0·1	0·2	0·3
Crude fibre .	9·9	8·6	0·4	0·3	5·9[1]
N-free extract .	8·3	10·4	—	—	70·0
Starch . .	—	—	19·1	—	
Dextrin . .	—	—	2·6	1·0	
Tannin . .	—	—	2·2	0·1	
Sucrose . .	—	—	—	15·8	
Invert sugar .	—	—	—	9·7	
Ash . . .	5·3	3·9	1·1	0·9	1·8

Only the quite green fruit, containing mere traces of sugar, can be used for preparing the meal.

Ripe bananas contain *invertase* (Mirran, Chem. Zeit. 1894, 17, 1283). American analyses show much less protein in ripe bananas than is given in Leuscher's figures, the average being only 1·3 p.c. (Bulletin 28, U.S. Dept. of Agriculture, 1899). H. I.

BAPTISIN *v.* GLUCOSIDES.

BARBALOIN *v.* GLUCOSIDES.

BARBATIC ACID. Barbatic acid $C_{19}H_{20}O_7$ was first isolated from the lichen *Usnea barbata* by Stenhouse and Groves (Chem. Soc. Trans. 1880, 37, 405) in which it occurs in conjunction with usnic acid. Zopf (Annalen, 1897, 297, 271) found barbatic acid in the *Usnea longissima*, in the *Electora ochroleuca* (*ibid.* 1899, 306, 282), and in the *Usnea dasypoga* (*ibid.* 1902, 324, 39); Hesse (J. pr. Chem. 1898 ii. 57, 232) describes its presence in the *Usnea longissima*, *Usnea barbata*, and *Usnea ceratina*. Hesse (*l.c.*) originally considered that barbatic acid had the composition $C_{22}H_{24}O_8$, and described potassium barium and copper salts and an ethyl ester m.p. 132, which apparently established this formula, but in a later paper (J. pr. Chem. 1903, ii. 68, 1) he confirms Stenhouse and Groves' formula, $C_{19}H_{20}O_7$. The *sodium salt* $C_{19}H_{19}O_7 \cdot Na, 2H_2O$ crystallises in straight-sided leaflets (compare also Zopf, 1902, 789). The action of acetic anhydride on barbatic acid leads to the formation of what is probably the lactone of acetylbarbatic acid; this melts at 250° and on recrystallisation from acetic anhydride yields *acetyl barbatic acid* $C_{19}H_{19}(C_2H_3O)O_7$, m.p. 172°. The hydrolysis of barbatic acid with aqueous alkalis yields *betorcinol* and *rhizoninic acid*. Barbatic acid crystallises in colourless needles, m.p. 184° (Hesse, J. pr. Chem. 1906 [2], 73, 113). A. G. P.

BARBERRY ROOT. The root of *Berberis vulgaris*, a wild shrub common to Europe and Asia. The active principle which it contains is the alkaloid *berberine* $C_{20}H_{17}NO_4, 5H_2O$, which may be prepared by boiling the root with water containing a slight excess of lead acetate, filtering, and evaporating the filtrate to crystallisation. Berberine crystallises in fine yellow prisms, very soluble in hot water and alcohol, but insoluble in ether. It begins to sublime at 200°. The salts of berberine are sparingly soluble. The hydrochloride and phosphate are used medicinally.

Berberine is also found in the root, wood, or bark of the following plants: *Berberis aristata*, *Berberis ætnensis*, *Zanthoxylum Clava-Herculis* (Linn.), *Hydrastis canadensis* (Linn.), *Coscinium fenestratum* (Colebr.), *Jateorhiza Columba* (Miers.), *Xylopia polycarpa* (Oliver), *Podophyllum peltatum* (Linn.), *Xanthorissa apiifolia*, *Coptis Teeta* (Wall.), *Soddalia aculeata*, *Evodia meliæfolia*.

The root, root-bark, and especially their concentrated liquid extracts, are used to a small extent for dyeing silk and leather yellow. It is the only natural basic colouring matter at present employed. Wool and silk are dyed in a neutral bath, or with a slight addition of alum to the dyebath. It gives somewhat clear yellow shades, not remarkable, however, for any special quality either of fastness or purity of colour.

Literature.—Buchner, Annalen, 24, 228; Fleitmann, *ibid.* 59, 160; Bœdeker, *ibid.* 66, 384; 69, 40; Dyson Perrins, *ibid.* Suppl. 2, 171, and 83, 276; Stenhouse, *ibid.* 95, 108. Repert. chim. appl. 4, 459; Repert. chim. pure, 3, 105; 4, 367; 5, 423; Annalen, 115, 132; 122, 256; Suppl. 1863, 2, 191; Journ. chim. med. 1826, 2, 314; Chem. Soc. Trans. 15, 339. Bull. Soc. Chim. 1863, 423; Chem. Soc. Abstr. 1885, 675; 1886, 633, 1041; 1887, 174, 383, 505, 1057; Chem. Soc. Trans. 1889, 63; Arch. Pharm. [3] 26, 329; 25, 164; Amer. J. Sci. [2] 33, 43; Annalen, 24, 228; Annalen, Suppl. 2, 197; Perkin and Hummel, Chem. Soc. Trans. 67, 415; Perkin, *ibid.* 71, 1195).

BARBITURIC ACID *v.* MALONYL CARBAMIDE.

BARILLA or BARILLOR. (Fr. *Barille.*) Commercial name of an impure soda obtained from the ashes of the *Salsola Soda* (Linn.), formerly grown specially in Spain, Sicily, Sardinia, the Canary Islands, and the Levant. The seed was sown at the end of the year, and the plants were ready for cutting in September of the following year; they were usually burnt during October. A hole capable of holding one or two tons of soda was dug in the ground and covered over with an iron grating; the dried plants, mixed with canes, were heaped on this and set on fire. The heat was sufficient to melt the ash, which ran down and collected in the hole. More material was supplied to the fire till the hole was full of fused soda; it was then covered with earth and left to cool, after which the porous mass was broken out and was ready for shipment. Contained about 20 p.c. alkali, together with chlorides and sulphates of sodium, calcium and aluminium and very little sulphur. Formerly much used for making soda soap; little, if at all, used now.

Kelp is sometimes called British Barilla.

BARIUM. Symbol, Ba. At. wt. 137·37.

The name 'barote' (from *βαρύς*, heavy) was given to the earth contained in heavy-spar (*terra ponderosa*) by Guyton de Morveau in 1779, and was afterwards altered to 'baryta' by Lavoisier; the name itself, therefore, is indicative of the great density of its compounds.

[1] Including tannin and colouring matter.

Barium occurs principally as the sulphate, *barytes* or *heavy-spar* $BaSO_4$, and is generally found associated with metallic ores containing sulphur. Dieulafait (Ann. Chim. Phys. [5] 15, 530) has shown that all primary rocks contain barium in sufficient quantity to be easily detected. Barium also occurs in nature as *witherite* $BaCO_3$, *barytocelestite* $(BaSrCa)SO_4$, *barytocalcite* $(BaCa)CO_3$, *alstonite* $(BaCa)CO_3$, and in certain varieties of the ores of manganese; also in certain silicates, as *brewsterite* $H_4(SrBa)Al_2Si_6O_{18},3H_2O$, *harmotome* $H_2(K_2Ba)Al_2Si_5O_{15}\cdot 4H_2O$, and *hyalophane* or *baryta-felspar* $K_2Ba\cdot 2Al_2Si_8O_{24}$, and frequently in mineral waters. Barium is also frequently found in calcium and strontium minerals, replacing a portion of those elements with which it is isomorphous.

It is never found native. Its oxide, baryta BaO, was first recognised as a peculiar earth distinct from lime by Scheele in 1774.

Preparation.—Davy (Phil. Trans. 1808, 354) electrolysed a moist paste of a barium salt, using a cathode of mercury. He thereby obtained a poor amalgam which on distillation yielded a silver-white solid that he believed to be metallic barium, but which in reality was only a rich amalgam as shown by Donath (Ber. 12, 745).

Bunsen (Pogg. Ann. 91, 619) slightly modified Davy's process, heating the amalgam in a charcoal boat in a current of hydrogen, obtaining a tumefied mass which was probably a mixture of hydride and carbide. Guntz has also shown that Kern's method (Chem. News, 31, 243) of heating the iodide with sodium yields a subiodide which decomposes water.

Clarke (Ann. Phil. 17, 419) exposed baryta to the action of the oxy-hydrogen blow-pipe flame on charcoal and obtained metallic-looking globules probably of barium carbide.

Matthiessen (Annalen, 93, 277) electrolysed the fused chloride and obtained metallic-looking globules which were probably subchloride.

Maquenne (Bull. Soc. chim. (3) 7, 368) heated the amalgam *in vacuo*, but owing to decrepitation of the substance and rupture of the tube he was unable to obtain satisfactory results.

Guntz (Bull. Soc. chim. [3] 29, 483), by studying the same process, was finally able to distil off all the mercury without decrepitation or bursting of the tube. After many experiments, he finally adopted the following method: An amalgam containing 3 p.c. of barium was prepared according to Davy's original process, and 5 to 6 kilos of it were distilled in an atmosphere of hydrogen under reduced pressure to such a point as to obtain an amalgam having a close grain and not readily oxidisable, containing about 10 p.c. barium. About half a kilo. of it was then placed in an iron boat contained in a large porcelain tube. Over the boat was placed a nickel spiral to prevent spurting and loss. The tube was then heated very slowly by an electric current circuit so as to arrive at a dull red heat in about four hours, a vacuum being maintained in the tube. The amalgam slowly loses mercury without change of form, and towards 900° it suddenly liquefies, when the current is turned off to avoid ebullition and loss. The amalgam so obtained, containing about 65 p.c. barium, has a coarsely faceted crystalline structure, and quickly oxidises in air. For the last operation it is placed in a nickel boat contained in a porcelain tube lined with nickel foil. The latter is necessary as when the barium distils towards the end of the operation its corrosive action on the glass causes rupture. The tube is maintained at 900° for two or three hours under diminished pressure, keeping the ends of the tube suitably cooled; then at 950° for one hour during which time there is a considerable loss of barium. The barium so obtained is kept in an atmosphere of dry carbon dioxide. A sample obtained by distilling half the barium had the composition Ba 98·35, Hg 0·83, Fe 0·40. In repeated experiments Guntz failed to obtain barium much purer than 98 p.c. He, however, found in his later experiments that by preparation of the hydride a much purer metal could be obtained (Compt. rend. 141, 1240). The method is a modification of the earlier experiment. After the preparation of the metal in the above way pure dry hydrogen is allowed to enter the tube, maintained at 900°. It is then heated to 1200°, just below the fusion point of the hydride; by this means every trace of mercury can be removed. The hydride contained in a nickel boat is then placed in the nickel-lined tube, heated in a vacuum at 1200°, whereby the hydride is completely decomposed and the volatilised barium is condensed on a polished steel tube cooled by circulating water placed inside where the vapours are being liberated. The metal so obtained assayed 99·5 p.c. barium and was free from hydrogen.

A very convenient laboratory method for preparing small quantities of barium, also due to Guntz, is to heat barium oxide with one-tenth its weight of metallic aluminium at 1200° in a vacuum. The metal condenses in the cooler part of the tube and assays as much as 98·8 p.c. barium.

The preparation of the metal by electrolysis of the fused oxide or chloride does not appear to be attended with success; sub-salts are formed, and the current passes without further action (Z. Electroch. 9, 291.)

Properties.—Barium when absolutely pure is a silver white metal with a density of 3·78. It is slightly harder than lead. It melts at about 850° and commences to volatilise at 950°. Barium oxidises rapidly in air yielding principally the monoxide; the powder easily takes fire spontaneously. Guntz states that molten barium attacked all the metals he tried, iron and nickel being the most resistant. Barium decomposes water and alcohol in the cold, yielding in the latter case barium ethoxide.

Oxides of barium. Three oxides of barium are known—barium suboxide Ba_2O, barium oxide or baryta BaO, and barium peroxide BaO_2.

Barium suboxide Ba_2O is obtained, according to Guntz (Compt. rend. 143, 339), by heating the protoxide with magnesium or barium to a temperature of 1100°. It is a black mass which decomposes water.

Barium oxide, protoxide, monoxide, or baryta, BaO, is the oxide formed when the metal burns in air. It is more readily obtained by heating (1) the nitrate or (2) the carbonate of barium.

(1) Barium nitrate heated progressively, fuses, then decomposes with the liberation of nitric fumes and much frothing leaving a porous mass of barium oxide.

(2) The carbonate may also be converted into barium oxide by exposing it to the strongest heat of a forge fire; but the last traces of carbonic acid are only expelled with difficulty. However, at an ordinary white heat, this may be accomplished by mixing the carbonate with one-tenth of its weight of lampblack or charcoal and making into a thick paste with oil or tar, carbonic oxide being evolved, thus:

$$BaCO_3+C=BaO+2CO.$$

The mixture should be heated in an earthen crucible lined with lampblack and fitted with a tight cover; on the large scale witherite is thus converted into baryta for use in separating crystallised sugar from molasses. In a second baryta-manufacturing process a mixture of the carbonates of barium and calcium is ignited in a current of aqueous vapour.

(3) On the small scale, baryta may be easily obtained by heating barium iodate, which readily gives up all its iodine, together with five-sixths of its oxygen, without fusing or frothing:

$$Ba(IO_3)_2=BaO+I_2O_5.$$

Barium oxide as prepared by the above methods is generally a greyish-white friable mass of specific gravity 4·7–5·5. Brügelmann (Annalen, [2] 4, 277), by heating barium nitrate in a porcelain flask, obtained minute crystals of BaO belonging to the regular system, of sp.gr. 5·722. He found later that by heating the oxide in a clay or graphite crucible he obtained needles belonging to the hexagonal system sp.gr. 5·32, but if heated in a platinum crucible the oxide is obtained in cubic forms, sp.gr. 5·74. It is therefore dimorphous (Zeitsch. anal. Chem. 29, 127). It is only just melted even by the heat of the oxyhydrogen blowpipe; but in the electric furnace it may be readily liquefied and volatilised. The liquid on cooling yields a crystalline mass (Moissan, Ann. Chim. Phys. [7] 4, 139); it is a non-conductor of electricity, but in presence of mercury may be electrolysed into barium and oxygen. BaO is strongly alkaline, caustic, and poisonous. Fluorine attacks it in the cold, liberating oxygen, the mass becoming incandescent. Dry chlorine has little or no action on the perfectly anhydrous baryta. It is deoxidised by potassium at a red heat, and slakes with water, forming barium hydrate $Ba(OH)_2$ with such energy that the whole mass becomes incandescent provided the amount of water be not too large. It rapidly absorbs moisture from the air. It unites with methyl and ethyl alcohols, forming the compounds $BaO,2CH_4O$ and $BaO,2C_2H_6O$. Heated in the vapour of carbon disulphide, it forms barium carbonate and barium sulphide:

$$3BaO+CS_2=BaCO_3+2BaS.$$

It dissolves readily in dilute nitric and hydrochloric acids, but with most other acids forms insoluble salts. When vapour of sulphuric anhydride is passed over it, heated to low redness in a glass tube, formation of barium sulphate $BaSO_4$ occurs with incandescence.

Barium peroxide or dioxide BaO_2 is formed when anhydrous baryta is heated to a dull red heat in a stream of oxygen or of air freed from carbonic acid. Barium hydroxide may be similarly converted into the peroxide, but less readily, as it fuses below the temperature of absorption of oxygen; but the absorption may be rendered rapid by mixing the hydroxide with lime or magnesia which prevents fusion and keeps the mass porous. Peroxide of barium may also be obtained by sprinkling red-hot baryta with four times its weight of powdered potassium chlorate in successive small portions; the potassium chloride simultaneously formed may be washed out with water, leaving the peroxide in the form of a hydrate.

The peroxide obtained by these means is not pure, being contaminated with a little unconverted barium oxide, iron, silica, and other substances derived from the preparing vessels. In order to purify it the finely powdered crude product is gradually added to an excess of dilute hydrochloric acid, avoiding any considerable rise of temperature; the crude substance dissolves, forming barium chloride and peroxide of hydrogen. The solution is filtered from insoluble matters and treated with baryta water until the silica and ferric oxide, together with a little hydrated barium peroxide, regenerated by action of the peroxide of hydrogen upon the barium hydroxide, are precipitated. The liquid is again filtered and then supersaturated with baryta. By this means the whole of the peroxide of hydrogen regenerates barium peroxide, which is precipitated in minute prisms or laminæ of the hydrate $BaO_2,8H_2O$, in which condition the peroxide is best preserved, and is a suitable form for use in the preparation of peroxide of hydrogen. On drying at 130° or at ordinary temperatures *in vacuo* it is converted into pure anhydrous barium peroxide.

Barium peroxide is a grey, impalpable powder, slightly more fusible than the monoxide. The temperature of dissociation depends upon the pressure. According to Le Chatelier (Compt. rend. 115, 654), the figures are as follows:—

Temp. C.°	520	555	650	670	720	735	750	775	785	790
Press. mm.	20	25	65	80	210	260	340	510	620	670

These pressures vary according to the degree of decomposition being highest at the commencement of the operation. Brin's method of preparing oxygen depends upon the above physical factors. The spongy protoxide of barium prepared as indicated above is placed in thin beds in iron retorts heated by special furnaces. The temperature is maintained as constant as possible between 500° and 600°. Air which has been freed from moisture and carbon dioxide by passing first over quicklime and then over caustic soda is forced by pumps through the retorts whereby the BaO is converted to BaO_2. The residual nitrogen is allowed to escape into the atmosphere. When the peroxidation is complete a set of valves places the retorts in connection with the exhaust pumps, the reduction of pressure causing liberation of oxygen. The first portions are allowed to escape until the pressure measures 65 cm. mercury, another set of valves then comes into play and automatically connects the retorts with the gasometer. The oxygen obtained is 97 to 98 p.c. pure. Barium peroxide is used in the preparation of hydrogen peroxide or dissolved in acidulated water as a bleaching agent.

Peroxide of barium is decomposed by sulphuretted hydrogen at ordinary temperatures, and when heated in a current of carbonic oxide it becomes white hot. It becomes incandescent when heated in sulphur dioxide. When treated with strong sulphuric acid at a temperature exceeding 70°, oxygen is given off; at lower temperatures the oxygen is mixed with ozone. When the peroxide is mixed with acidulated water in presence of oxide of silver, peroxide of manganese, or peroxide of lead, oxygen is evolved both from the peroxide of barium and from the other oxide. A small quantity of a silver compound is capable of decomposing a large quantity of barium peroxide, but iodine decomposes an exactly equivalent quantity:

$$BaO_2+I_2=BaI_2+O_2.$$

The amount of active oxygen in BaO_2 may be determined by adding a known quantity of the peroxide to pure hydrochloric acid, then potassium iodide free from iodate together with excess of bicarbonate of soda, and titrating the liberated iodine with a standard solution of sodium thiosulphate. It may also be estimated by titrating an acidulated solution with standard potassium permanganate (Bertrand, Bull. Soc. chim. [2] 33, 148).

Barium hydroxide, *Hydrate of Baryta*, or *Caustic Baryta* $Ba(OH)_2$ or $BaO\cdot H_2O$, is formed, with great evolution of heat, when water is added to anhydrous baryta (barium oxide):

$$BaO+H_2O=Ba(OH)_2.$$

A hot concentrated solution of equivalent quantities of barium nitrate and sodium or potassium hydroxide deposits, on cooling, crystals of barium hydroxide. Soda is usually employed, of sp.gr. 1·10–1·15, and the crystals obtained are freed from mother liquor by draining, or better, by means of a centrifugal machine.

Commercial caustic baryta is prepared on the large scale by igniting the native sulphate or heavy spar with coal or charcoal, whereby an impure barium sulphide is obtained, and heating this in earthenware retorts into which a current of moist carbonic acid is passed, thus converting it into carbonate:

$$BaS+CO_2+H_2O=BaCO_3+H_2S.$$

Superheated steam is then passed over the heated carbonate, when the following decomposition takes place:—

$$BaCO_3+H_2O=Ba(OH)_2+CO_2.$$

According to R. Heintz (Chem. Zeit. 1901, 199), only the carbonate is used to any extent. The calcination is conducted in specially constructed furnaces lined with basic material and heated with producer gas. The product contains 95 p.c. BaO. The same author reviews the methods that have been suggested for the manufacture of baryta from barytes, and considers them too costly for the production of a cheap commercial oxide.

Caustic baryta crystallises from water in large, transparent, colourless, quadratic prisms capped by pyramids. The crystals $Ba(OH)_2$, $8H_2O$ are isomorphous with the corresponding strontium compound. They dissolve in 20 parts of water at 15°, and in 2 parts of boiling water. The aqueous solution known as baryta water is highly caustic and of strong alkaline reaction, rapidly becoming covered with a film of carbonate owing to absorption of atmospheric carbonic acid; hence it is frequently used in the determination of the amount of carbonic acid contained in the air. On exposure to air the crystals fall to a white powder, with loss of seven molecules of water. De Forcrand (Compt. rend. 103, 59) isolated the hydrate $Ba(OH)_2,H_2O$ by allowing the compound $BaO,2CH_3O+2H_2O$ to evaporate over sulphuric acid *in vacuo*. H. Lescœur (Compt. rend. 96, 1578) shows that at 100° $Ba(OH)_2,H_2O$ has a tension of dissociation of 45 mm., and that this hydrate is completely converted to $Ba(OH)_2$ when heated to 100° *in vacuo*. Lescœur also proves that the dissociation tension of $Ba(OH)_2,8H_2O$ is 213 mm. at 75°, so that at this temperature all three hydrates of BaO may exist simultaneously. $Ba(OH)_2$, when heated alone, is only reduced to baryta above a red heat; if not heated above redness, it re-forms, on cooling, a crystalline mass of $Ba(OH)_2$, but when heated in a current of air it takes up oxygen and is converted into peroxide of barium with loss of water; when heated in a current of carbonic acid it also loses water and is converted into barium carbonate:

$$Ba(OH)_2+O=BaO_2+H_2O.$$
$$Ba(OH)_2+CO_2=BaCO_3+H_2O.$$

Baryta has until recently been used in the processes of sugar-refining, inasmuch as it forms the compound $C_{12}H_{22}O_{11}BaO$ with cane-sugar, which, when treated with carbonic acid gas, is decomposed into insoluble barium carbonate and sugar, hence affording a means of separating the pure sugar from the molasses; but as strontium hydrate acts in a similar manner, and is not poisonous, it has been substituted for baryta in sugar-refining.

Hydrated barium peroxide. Schöne has shown (*Ber.* 13, 803) that only one hydrate of BaO_2 exists, containing 8 molecules of water, $BaO_2,8H_2O$. This hydrate is precipitated in crystalline scales when peroxide of hydrogen is added to concentrated solutions of barium hydroxide. It is slightly soluble in cold water, but decomposes in boiling water, forming $Ba(OH)_2$ and evolving oxygen.

Barium subchloride BaCl is obtained (Guntz, Bull. Soc. chim. [3] 29, 490) when equal amounts of $BaCl_2$ and Ba are heated together *in vacuo* at 850°. The fragments of $BaCl_2$ absorb the molten barium without change, and are microcrystalline. The material so obtained is not pure. It decomposes water. By using Na, a definite compound NaClBaCl can be obtained. BaCl appears to be formed when electrolysing fused $BaCl_2$.

Barium chloride $BaCl_2$. Crystallised (*terra ponderosa salita*) $BaCl_2,2H_2O$. Barium chloride may be prepared either from witherite, the native carbonate, or from heavy-spar, the native sulphate. The witherite is dissolved in dilute hydrochloric acid and the solution allowed to stand some time in contact with excess of the carbonate, which is added to precipitate iron and other foreign metals present in the mineral; the rapidity of precipitation is much increased by the addition of a little baryta water. The filtered liquid is then neutralised with hydrochloric acid, and the salt crystallised out and purified by recrystallisation.

From the native sulphate barium chloride may be prepared in two ways:

(1) By heating the sulphate in a crucible with

powdered coal and decomposing a filtered solution in water of the barium sulphide formed with hydrochloric acid: $BaS+2HCl=BaCl_2+H_2S$.

Excess of hydrochloric acid is added, and the liquid boiled till free from sulphuretted hydrogen; it is then filtered, cooled, and evaporated to the crystallising point.

(2) By heating a mixture of 100 parts finely powdered heavy-spar, 40 parts of charcoal, 20 parts of limestone, and 50 parts of calcium chloride to a red heat in a reverberatory furnace, by which barium chloride and calcium sulphide are formed. The mass is lixiviated with water, when the barium chloride is dissolved out, leaving an insoluble calcium oxysulphide formed by the union of the sulphide with the oxide of calcium produced by ignition of the limestone.

In this process the manganese chloride left as a by-product of the chlorine manufacture may be used in place of calcium chloride, a little sand being added along with the limestone or chalk, and heated on a cast-iron plate. Wackenroder (Dingl. poly. J. 253, 440) has proposed to prepare barium chloride by adding an equivalent of calcium chloride to a solution of barium sulphide, and passing a stream of carbonic acid gas into the mixture, whereby calcium carbonate is precipitated.

Commercial barium chloride generally contains small quantities of strontium and calcium chlorides, together with traces of the chlorides of iron, aluminium, copper, and lead. Washing the crystals with alcohol removes both the strontium and calcium chlorides, whilst calcium chloride may also be removed by digesting with barium carbonate suspended in water, when the calcium chloride becomes converted to carbonate, or more rapidly by adding baryta water and passing carbonic acid gas into the liquid. Digestion with barium carbonate also precipitates the sesquioxides of iron and alumina. Lead and copper may best be removed by the addition of a little barium sulphide.

Barium chloride may be recovered from mixtures of chlorides of the alkalis and alkaline earths by treating the concentrated liquor with a hot saturated solution of salt, when on cooling a mixture of barium and sodium chlorides crystallises out; by treating a cold saturated solution of this mixture with twice its volume of hydrochloric acid, barium chloride is precipitated (Dingl. poly. J. 250, 91).

Barium chloride crystallises from aqueous solution with two molecules of water $BaCl_2,2H_2O$ in transparent, colourless, rhombic tables; sp.gr. 2·66–3·05. The crystals decrepitate when heated. They have an unpleasant, bitter, sharply saline taste, exciting nausea, and are very poisonous.

One hundred parts of water at 0° dissolve 32·62 parts of anhydrous barium chloride, and 0·2711 part for every degree above 0°; 100 parts of water at 15·6° dissolves 43·5, and at 105·5° 78 parts of the crystallised chloride. One part of crystallised barium chloride at 18·1° dissolves in 2·257 parts of water to form a solution of sp.gr. 1·28251 (Karsten). A solution saturated at 8° has a sp.gr. of 1·270 (Anthon).

Barium chloride is almost insoluble in strong hydrochloric acid, so that it is precipitated from its solutions by hydrochloric acid, and a few drops of the acid reduces the solubility considerably. Hot absolute alcohol dissolves only $\frac{1}{450}$ part of the crystals; but according to Fresenius, 1 part of the salt dissolves in 8108 parts of alcohol of 99·3 p.c. at 14°, and in 4857 parts of the same alcohol at its boiling point.

The crystals are not efflorescent, but give up the whole of their water at 100°, leaving a white mass of the anhydrous salt, which melts at a red heat, forming a translucent mass on cooling. Specific gravity of the anhydrous chloride is given by various observers as 3·70 to 4·15. When heated in a current of steam it evolves hydrochloric acid below its fusing point.

A concentrated solution of barium chloride is decomposed by sodium or potassium nitrate forming barium nitrate and a chloride of the alkali-metal. With glycocol $CH_2(NH_2)\cdot COOH$ it forms a crystalline compound, and also acts upon blood as a preventive of putrefaction and coagulation.

Barium chloride is extensively used as a reagent, especially for the detection and estimation of sulphuric acid. It is also used for the preparation of artificial sulphate or 'permanent white,' and for preventing the incrustation of steam boilers by decomposing the gypsum of hard waters.

Barium oxychloride. André (Compt. rend. 93, 58) obtained an oxychloride of barium by adding 60 grams of $Ba(OH)_2$ to 200 grams of crystallised barium chloride, and boiling the mixture with 500 grams of water, filtering, and allowing to cool, when nacreous lamellæ, to which he ascribed the formula $BaCl_2\cdot BaO,5H_2O$, separated out (Compt. rend. 98, 572). Beckmann (J. pr. Chem. [2] 27, 126) also obtained nacreous plates by similar means to which he gave the formula $BaCl(OH),2H_2O$. These plates lose $\frac{4}{5}$ths of their water at 120° and the remaining fifth at the fusing-point by prolonged heating in a stream of hydrogen. This oxychloride is readily decomposed by water or alcohol.

Barium chlorate $Ba(ClO_3)_2$. Dry $Ba(OH)_2$ does not absorb chlorine, but in presence of water it rapidly takes it up, forming first hypochlorite and chloride, the former of which breaks up into chlorate and chloride

$$6BaO+6Cl_2=5BaCl_2+Ba(ClO_3)_2$$

(Konigel-Weisberg, Ber. 12, 346).

As it is difficult to separate from the chloride, the chlorate is best prepared by neutralising a solution of chloric acid with barium carbonate and evaporating to the crystallising point. It crystallises in colourless monoclinic prisms with 1 molecule of water, soluble in 4 parts of cold and less than 1 part of boiling water.

Barium chlorate is also slightly soluble in alcohol, and the alcoholic solution burns with a green flame.

If strongly heated fused barium chlorate be plunged into a jar of coal gas, a brilliant combustion of the carbon and hydrogen contained in the coal gas occurs at the expense of the oxygen of the chlorate.

Barium perchlorate $Ba(ClO_4)_2,4H_2O$ is readily formed by neutralising perchloric acid with barium hydrate or carbonate. It crystallises from the solution in long deliquescent prisms very soluble in water.

Barium bromide $BaBr_2$. Crystallised $BaBr_2,2H_2O$.

This salt is prepared by saturating baryta water or barium carbonate or sulphide with hydrobromic acid; or by decomposing the sulphide with free bromine, sulphur being precipitated.

The most convenient method is to bring together under water 12·5 parts of bromine and 1 part of amorphous phosphorus, by which a solution of hydrobromic and phosphoric acids is formed, which is neutralised with barium carbonate rendered alkaline by baryta water. The insoluble barium phosphate may then be filtered off and the bromide obtained by evaporation and crystallisation.

Barium bromide is very soluble in water, and crystallises with difficulty; it is isomorphous with the chloride, but unlike the latter salt is soluble in strong alcohol. It loses one molecule of water at 75°, and the second at 120° (Beckmann, J. pr. Chem. [2] 27, 126).

Barium oxybromides. Two oxybromides have been prepared by Beckmann (*l.c.*).

$BaBr(OH),2H_2O$ resembles the corresponding oxychloride. $BaBr(OH),3H_2O$ was obtained by adding alcohol to mixed solutions of $BaBr_2$ and $Ba(OH)_2$.

Barium iodide BaI_2. Crystallised $BaI_2,7H_2O$. Barium iodide is formed when hydriodic acid gas is passed over baryta at a red heat, a violent action occurring attended with incandescence. It is generally prepared by mixing barium monosulphide with a saturated solution of iodine in alcohol as long as sulphur is precipitated; the filtrate is then boiled rapidly to near dryness, redissolved in a little water and again evaporated, this time to dryness, preventing the access of air as much as possible by performing the operation in a glass bolt-head. On redissolving the mass in hot water and allowing to cool, slender needles separate out of the composition $BaI_2,7H_2O$ (Croft, Gazz. chim. ital. 1856, 125; Thomsen, Ber. 10, 1343).

These crystals are very deliquescent and readily soluble in alcohol. They lose 6 molecules of water at 125°, and the remainder at 150° (Beckmann, J. pr. Chem. [2] 27, 126). They decompose slowly at ordinary temperatures, and quickly when warmed, giving off violet vapours of iodine.

The double iodide of barium and mercury has a sp.gr. of 3·588 higher than that of Thoulet's solution, and may be of use for petrographical purposes (Rohrbach, Jahrb. Min. 1883, 2, Mem. 186).

Barium oxyiodide. Beckmann (J. pr. Chem. [2] 27, 126) prepared an oxyiodide of barium of the formula $BaI(OH),4H_2O$ which crystallises in short thick needles.

Barium iodate $Ba(IO_3)_2$ is largely used for the preparation of iodic acid, and is obtained as a white granular precipitate by adding potassium iodate to barium chloride.

It is soluble in 3000 parts of cold and 600 parts of boiling water. It dissolves in hot nitric acid, and crystallises out on cooling in bright, glittering, monoclinic prisms isomorphous with the chlorate. Hydrochloric acid dissolves it with evolution of chlorine.

Barium periodate. By passing iodine vapour in a current of dry air over heated oxide of barium a basic periodate of the formula $Ba_5I_2O_{12}$ or $Ba(IO_4)_2{\cdot}4BaO$ is formed. The same basic periodate is formed when barium iodate is heated to a high temperature:

$$5Ba(IO_3)_2 = Ba_5I_2O_{12} + 4I_2 + 9O_2$$

or on heating barium iodide in a current of air until no more iodine is given off:

$$5BaI_2 + 6O_2 = Ba_5I_2O_{12} + 4I_2.$$

Hence Sugiura and Cross (J. Chem. Soc. 1879, 118) conclude that $Ba_5I_2O_{12}$ is the most stable combination of barium, iodine, and oxygen.

Barium fluoride BaF_2 is obtained by neutralising hydrofluoric acid with barium hydroxide or recently precipitated carbonate; or by precipitating a solution of barium nitrate with sodium or potassium fluoride. It forms a white, granular, crystalline powder, sparingly soluble in water, but readily soluble in nitric, hydrochloric, or hydrofluoric acids.

It combines with fluorides of silicon and boron, forming the compounds $BaF_2{\cdot}SiF_4$ barium silicofluoride and $BaF_2{\cdot}2BF_3$. The former is precipitated by adding hydrofluosilicic acid to soluble barium salts as a crystalline precipitate totally insoluble in alcohol, and serves as a means of separating barium from strontium and calcium, which are not precipitated by hydrofluosilicic acid.

Barium fluoride forms a crystalline compound with the chloride of barium $BaCl_2{\cdot}BaF_2$ when a solution of barium chloride is mixed with one of sodium or potassium fluoride; this double compound is more stable than the fluoride itself, and remains as a granular mass on evaporation of the solution.

Barium carbide BaC_2 was first obtained by Maquenne (Ann. Chim. Phys. (6) 28, 259) by heating a mixture of the carbonate and carbon with magnesium or by the action of carbon on the amalgam in an atmosphere of hydrogen at a red heat. Moissan (Compt. rend. 118, 683) obtained it in a pure crystalline condition by heating a mixture of the carbonate or the oxide with carbon in an electric furnace. Its specific gravity is 3·75; and it possesses properties similar to CaC_2, but is more fusible.

Barium carbonate $BaCO_3$. The native carbonate was first noticed to occur at Leadhills in Scotland, in 1783, by Withering, and hence received the name *witherite*. It is found in many places in England, specially fine crystals being met with at Fallowfield in Northumberland: it is also found in Silesia, Hungary, Styria, Russia, South America. Witherite crystallises in the rhombic system isomorphous with aragonite. It occurs also in globular, tuberose, and botryoidal forms; more frequently massive. Sp.gr. 4·29–4·35; hardness 3–3·75.

Knop (Landw. Versuchs-Stat. 17, 65) found 0·02 p.c. of barium carbonate in Nile mud from Minich and Achmin; and Dworzack (Landw. Versuchs-Stat. 17, 65) found baryta in the ash of the wheat grown thereon. *Alstonite* $(BaCa)CO_3$ contains barium and calcium in varying proportions, and is isomorphous with witherite. *Baryto-calcite* $BaCO_3 + CaCO_3$ crystallises in the monoclinic system.

Barium carbonate is rapidly formed when baryta, hydrated or anhydrous, is exposed to the atmosphere. When BaO is heated in CO_2 it absorbs the gas, becoming incandescent; the basic carbonate being formed (Raoult, Compt. rend. 92, 1, 110).

It is readily prepared by precipitating aqueous solutions of the nitrate or chloride with ammonium carbonate, filtering, and washing with hot water; or by igniting a mixture of 10 parts powdered heavy-spar, 2 parts charcoal, and 5 parts pearl ash (potassium carbonate). Potassium sulphide and barium carbonate are obtained and may be separated by water. The impure carbonate thus produced may be used to prepare other salts of barium, but these salts will contain iron.

Artificial barium carbonate is a dense soft white powder, poisonous, and hence used for destroying rats. It is very sparingly soluble in water, slightly soluble in water containing carbonic acid, owing to the formation of an acid carbonate which is stable only in solution. It dissolves readily in ammonium chloride, nitrate, and succinate, and when boiled with ammonium chloride is totally decomposed, forming ammonium carbonate and barium chloride.

It is not decomposed at a strong red heat, but at the heat of a forge fire it fuses with loss of carbon dioxide; the tension of CO_2 emitted at 1100° is 20 mm.; at 1600° dissociation is complete. The decomposition is much more easily effected in presence of carbon, being complete at 1450°. It is decomposed by steam at a red heat, and very easily if mixed with an equal weight of chalk or slaked lime.

The artificial carbonate is of considerable use in chemical analysis.

Barium nitride Ba_3N_2. Maquenne (Bull. Soc. chim. [3] 7, 368) obtained this compound by passing nitrogen into a tube containing a 25 p.c. amalgam at a red heat. Guntz and Mentrel (*ibid.* (3) 29, 581) obtained it by heating barium ammonium at 430°. So obtained it is a light porous material of a canary-yellow colour. It decomposes water in the cold, giving ammonia and $Ba(OH)_2$.

Barium ammonium is formed by the action of ammonia gas on barium or barium amalgam below 28°; but it is best prepared by dissolving barium in dry liquid ammonia at −50°, when it forms a dark-blue oily liquid immiscible with the liquid ammonia. The compound is somewhat indefinite, but a body having the formula $Ba(NH_3)_6$ appears to exist.

Barium amide $Ba(NH_2)_2$ is obtained by heating barium ammonium to 60° or by passing ammonia over barium at 280°C.

Barium nitrite $Ba(NO_2)_2,H_2O$ is prepared by heating the nitrate, dissolving in water, and precipitating any baryta formed by passing a stream of carbonic gas through the solution, adding alcohol to the filtrate to precipitate the unreduced nitrate, and evaporating to the crystallising point. Or by passing nitrous vapours into baryta water, evaporating to dryness, digesting in a small quantity of water (not sufficient to dissolve the nitrate) and crystallising. It is most readily prepared pure by adding barium chloride to a boiling solution of silver nitrite, filtering off the silver chloride, and evaporating.

It is permanent in the air, readily soluble in water or alcohol, and crystallises in colourless prisms, either needle-shaped or, according to Fischer, thick short prisms of 71¾°.

Barium nitrate $Ba(NO_3)_2$. A native barium nitrate has been discovered in Chili in the form of colourless octahedra, occasionally twinned like spinelle (Groth, Jahrb. Min. 1883, 1, Ref. 14).

Barium nitrate is prepared on the large scale either by dissolving the native carbonate (witherite) or the crude sulphide in dilute nitric acid, or by mixing hot saturated solutions of barium chloride and sodium nitrate. On cooling, the larger portion of the barium nitrate crystallises out, and the evaporation of the mother liquors yields the remaining portion.

Barium nitrate crystallises in lustrous, colourless, regular octahedra, frequently modified by faces of the cube, of sp.gr. 3·2. The crystals are permanent in the air, decrepitating when heated, and melting at 597° (Carnelley). At a red heat the salt decomposes, evolving oxygen, nitrogen, and nitrogen peroxide, and leaving a residue of pure baryta. It detonates slightly with combustible bodies, and decomposes with a yellowish light when thrown upon the fire. It is largely used in pyrotechny for giving green-coloured lights, especially for the preparation of green fire; and for the manufacture of *saxifragin*, an explosive mixture of 76 parts of barium nitrate, 2 parts of nitre, and 22 parts of charcoal.

It dissolves in water, producing a slight depression of temperature; 100 parts of water dissolve 5·2 parts of barium nitrate at 0°, 9·2 at 20°, 17·1 at 50°, and 32·2 at 100°. It is less soluble in dilute nitric acid; hence a second crop of crystals may be obtained from cooled saturated solutions on addition of a little nitric acid. It is quite insoluble in concentrated nitric acid and in alcohol.

Hirzel (Zeitsch. f. Pharm. 1854, 49) obtained a hydrate $Ba(NO_3)_2,2H_2O$ from a solution cooled below 12°. Berry (Chem. News, 44, 190), by saturating the same water with barium and strontium nitrates, introducing a crystal of $Sr(NO_3)_2,4H_2O$, and evaporating over sulphuric acid *in vacuo*, obtained crystals containing 17 p.c. of a hydrated barium nitrate isomorphous with the strontium compound.

Barium monosulphide BaS is obtained in a pure state by passing sulphuretted hydrogen over heated baryta as long as water is formed. Veley (Chem. Soc. Trans. 1886, 369) prepared pure crystals of the hydrate of barium hydroxide $Ba(OH)_2,8H_2O$, and heated them at 80° in a current of hydrogen until they attained the constant composition $Ba(OH)_2,H_2O$, when a stream of sulphuretted hydrogen was passed over them, yielding pure BaS and water:

$$Ba(OH)_2,H_2O+H_2S=BaS+3H_2O.$$

It may also be prepared by passing carbon disulphide over red-hot baryta, or by reducing powdered barium sulphate in a stream of hydrogen.

On the manufacturing scale it is prepared by roasting 100 parts of heavy-spar with 20 parts of coal slack or charcoal. If charcoal is used, a thorough mixture must be effected, as the reaction is otherwise very imperfect, owing to the non-fusibility of the mass. If the slack of bituminous coal is used, the 'caking' supplies a carbonaceous material which readily permeates the mass and ensures complete reduction. The admixture of resin, oil, or sawdust is also advantageous, and the asphalt of gas works is a capital reducing material, as the hydrogen contained in it prevents the formation of polysulphides of barium. The mass thus obtained

contains excess of carbon and some undecomposed sulphate, but the barium sulphide may be extracted by treating with hot water.

Another method is to heat a mixture of 100 parts heavy-spar, 200 of common salt, and 15 parts charcoal powder in a reverberatory furnace, the salt being added to assist fusion.

Barium sulphide forms a white mass of hepatic odour and alkaline taste, soluble in water, forming a mixture of hydrate and sulphydrate:

$$2BaS+2H_2O=Ba(SH)_2+Ba(OH)_2.$$

When exposed to the air it becomes converted into carbonate with evolution of sulphuretted hydrogen, owing to absorption of moisture and carbonic acid. When heated to redness in presence of aqueous vapour, it is converted into barium sulphate with elimination of hydrogen. It is decomposed by hydrochloric and nitric acids with formation of the chloride and nitrate and elimination of sulphuretted hydrogen. Chlorine, bromine, and iodine decompose it with formation of chloride, bromide, and iodide, and deposition of sulphur.

The phosphorescent material known as 'Bolognian phosphorus' is a sulphide of barium obtained by heating 5 parts of precipitated barium sulphate with 1 part of powdered charcoal over a gas flame for half an hour, and then heating for ten minutes over the blowpipe; it must be sealed up while still hot in glass tubes. After exposure to the sun's rays, or to any light rich in ultra-violet rays such as that emitted by burning magnesium wire or the electric arc, it phosphoresces in the dark with a brilliant orange-coloured light. Sulphides of barium, strontium, and calcium are now manufactured for the preparation of luminous paints which are used for coating clock-faces, match-boxes, &c. Their surfaces are protected from moisture by a thin coating of varnish. Barium sulphide is now largely used in the manufacture of lithophone by adding it dissolved in water to a solution of zinc sulphate. Mutual precipitation takes place, and the white powder formed, consisting of zinc sulphide and barium sulphate, is used as a rubber filler.

When a solution of 5 parts of barium sulphide is boiled with 1 part of sulphur, and the solution evaporated over sulphuric acid *in vacuo*, colourless six-sided transparent tables of $BaS,6H_2O$ are deposited, which are decomposed by a small quantity of water, forming barium hydrosulphide which dissolves, and barium hydroxide which remains behind.

Barium hydrosulphide $Ba(SH)_2$ is formed by saturating a warm solution of barium hydroxide or sulphide with sulphuretted hydrogen, evaporating apart from the air and cooling, when crystals of baryta and yellow prisms separate out. The mother liquor is mixed with alcohol, filtered from the sulphur and barium thiosulphate formed, and cooled to −10°, when colourless transparent four-sided prisms are obtained. The crystals contain water, which they lose on heating, becoming white. Exposure to air decomposes the crystals, with efflorescence, into barium thiosulphate and sulphate. Heated in a retort, they lose their water of crystallisation without fusing, evolving sulphuretted hydrogen as the temperature approaches redness, and leaving a yellow mass of barium monosulphide, which becomes white on cooling. It is insoluble in alcohol.

Veley (Chem. Soc. Trans. 1886, 369) finds that the composition of crystals of barium sulphydrate is $Ba(SH)_2,4H_2O$.

Barium trisulphide BaS_3 is formed as a greenish-yellow mass when 2 parts of barium sulphide are fused with 1 part of sulphur, the excess of sulphur being distilled off below 360°. It melts at 400° with loss of sulphur and formation of a black liquid. On boiling for some time with water it dissolves to a red liquid which deposits on cooling crystals of the hydrated mono- and tetrasulphides of barium.

Barium tetrasulphide BaS_4. When 7 parts of barium sulphide are boiled in water with 4 parts of sulphur, pale-red rhombic prisms are deposited, soluble in water to a red-coloured liquid from which alcohol precipitates it as an orange-coloured crystalline powder.

Veley (Chem. Soc. Trans. 1886, 369) obtains it by dissolving sulphur in a warm saturated solution of barium hydrosulphide; the crystals which separate out have the composition $BaS_4,2H_2O$.

Barium pentasulphide BaS_5 is obtained in solution by boiling an aqueous solution of the monosulphide with sulphur. On evaporation of the caustic alkaline yellow solution, crystals of barium tetrasulphide and sulphur are obtained: $BaS_5=BaS_4+S$.

Barium sulphocarbonate $BaCS_3$ is deposited as a canary-yellow crystalline powder when a solution of barium sulphide is added to carbon disulphide (Thenard, Compt. rend. 79, 673). On the large scale 90 p.c. yield may be obtained, and Dumas suggested its use against the phylloxera in wine districts. Thenard was of opinion that this barium salt would be injurious to the soil, and proposed to convert it into the potassium salt by adding potassium sulphate to its solution.

Barium sulphite $BaSO_3$ is obtained as a white crystalline precipitate by adding potassium or sodium sulphite to a soluble barium salt. Is soluble in a warm solution of sulphurous acid, and crystallises out on cooling in six-sided prisms. When heated in closed vessels it is converted into a mixture of sulphide and sulphate, but heated in air the sulphate is the sole product. Birnbaum and Wittich (Ber. 13, 651) state that BaO unites slowly with SO_2 at 200°, but more rapidly at 230°, forming $BaSO_3$.

Barium sulphate $BaSO_4$ occurs in nature as *barytes*, or heavy-spar, forming fine tabular crystals belonging to the rhombic system. It is a very common mineral in metalliferous veins, and is more particularly associated with lead, silver, and cobalt ores. Clowes (Chem. News, 52, 194) states that the beds of the new red sandstone near Nottingham are permeated by minute crystals of heavy-spar, which acts as a cementing material.

Crystals of artificial barytes, identical in form and properties with native heavy-spar, may be obtained by fusing certain metallic chlorides, such as those of manganese, sodium, potassium, or even barium itself, gradually dissolving barium sulphate in the fused mass, very slowly cooling, and afterwards extracting the soluble chlorides with water. By this means Gorgeu (Compt. rend. 96, 1734) prepared crystals much larger than those obtained by the older process

of fusing potassium sulphate with barium chloride. The sp.gr. of the mineral and of the artificial crystals varies from 4·3 to 4·7.

Barium sulphate has been formed by Spring (Bull. Soc. chim. 46, 299) by subjecting an intimate mixture of molecular proportions of sodium sulphate and barium carbonate to great pressure. It is precipitated as a heavy white amorphous powder of sp.gr. 4·0–4·5, when sulphuric acid or a soluble sulphate is added to the solution of a barium salt; this precipitate is insoluble in water, very slightly soluble in dilute acids, more so in strong acids. Concentrated sulphuric acid does not attack anhydrous baryta, but pyrosulphuric acid attacks it so violently that the mass becomes incandescent, and forms barium sulphate. When freshly precipitated, it is readily soluble in concentrated sulphuric acid at 100°, the solution depositing on cooling lustrous prisms of the *acid barium sulphate* $BaH_2(SO_4)_2$. If the acid solution be exposed to the air, moisture is taken up, and silky needles of a salt having the composition $BaH_2(SO_4)_2,2H_2O$ are deposited. Both these acid salts are decomposed by water, yielding sulphuric acid and the neutral salt.

Barium sulphate is also soluble to a perceptible extent in ammonium nitrate. Hydrobromic acid solution containing 40 p.c. HBr dissolves it to the extent of 1 in 2500 parts acid (Haslam, Chem. News, 53, 87).

Barium sulphate is partially decomposed by boiling with a concentrated solution of a fixed alkaline carbonate into alkaline sulphate and barium carbonate, but the reaction is much more complete when the sulphate and alkaline carbonate are fused together. It is reduced to sulphide by ignition with charcoal or organic matter, also by ignition in a stream of coal gas or of hydrogen mixed with vapour of carbon disulphide.

Powdered heavy-spar is used to adulterate white lead, but has not sufficient body to form a pigment by itself; the amorphous sulphate is prepared on the large scale by precipitation of a solution of barium chloride of sp.gr. 1·19 by one of sulphuric acid of sp.gr. 1·245, and is used as a pigment under the name of 'permanent white' or 'blanc fixe.'

Barium sodium sulphate $BaNa_2(SO_4)_2$ is formed as an opaque hard mass of pearly lustre by fusing together equivalent quantities of the sulphates of sodium and barium (Berthier).

Barium disulphate BaS_2O_7. If precipitated, barium sulphate be dissolved in fuming sulphuric acid, and the solution heated to 150°, on cooling a glistening deposit of granular crystals of the disulphate is obtained. Decomposition of these crystals occurs at a low red heat without previous fusion.

Barium dithionate $BaS_2O_6,2H_2O$. Prepared by adding barium sulphide to the manganese salt formed on passing sulphur dioxide through finely divided manganese dioxide suspended in water:

$$MnS_2O_4+BaS=MnS+BaS_2O_6.$$

On allowing the solution to evaporate in a warm place, glittering monoclinic crystals of the salt are deposited of the composition BaS_2O_6, $2H_2O$. According to Sénarmont and Rammelsberg, the crystals are rhombic. According to V. Lang (Sitz. B. [2] 45, 27), they are monoclinic.

The crystals are soluble in 4 parts of water at 18° and in 1·1 parts at 100°. When the dry salt is heated, it breaks up into sulphur dioxide and barium sulphate. The same decomposition occurs on boiling with hydrochloric acid, but the solution of the dithionate itself in water may be boiled without decomposition.

A tetrahydrate $BaS_2O_6,4H_2O$ may also be obtained by spontaneous evaporation in distinct shining monoclinic crystals, which effloresce on exposure to air.

Barium thiosulphate

$$BaS_2O_3,H_2O \text{ or } BaH_2(SO_2)_2$$

is obtained as a white crystalline precipitate when the sodium salt $Na_2S_2O_3$ is added to barium acetate; it loses its water of crystallisation at 215°. The anhydrous salt, when heated to redness, gives off sulphur and leaves a residue of barium sulphide, sulphite, and sulphate:

$$6BaS_2O_3=BaS+2BaSO_3+3BaSO_4+6S.$$

Barium selenide BaSe is formed by heating barium selenite to redness in a stream of hydrogen. It is decomposed by water into barium hydroxide and a higher selenide, which is decomposed by acids with evolution of H_2Se and precipitation of selenium.

Barium selenate $BaSeO_4$ resembles the sulphate in being insoluble in water, but differs from it in being decomposed by hydrochloric acid into selenite, which dissolves in the hydrochloric acid.

Barium chromate $BaCrO_4$ is precipitated as a yellow crystalline powder when potassium chromate or bichromate is added to the solution of a barium salt. The salt may be obtained in green rhombic crystals isomorphous with $BaSO_4$ by heating two equivalents of $BaCl_2$ with one equivalent of potassium chromate and one of sodium chromate, and allowing the mixture to cool; the chlorides may be boiled out with water, leaving the right rhombic prisms of $BaCrO_4$, of sp.gr. 4·6. They are insoluble in water, but are easily soluble in hydrochloric and nitric acids, and are decomposed by sulphuric acid into $BaSO_4$ and CrO_3 (Bourgeois, Compt. rend. 88, 382).

The precipitated chromate is used as a pigment under the name of 'lemon yellow' or 'yellow ultramarine.' When strong sulphuric acid is added to the dry pigment, great heat is developed, and it is coloured deep red from liberation of CrO_3. If it be now ground in a mortar and heated to bright redness, the chromic acid is reduced to chromic oxide, and a fine green pigment is obtained (Douglas, Chem. News, 40, 59).

Barium dichromate $BaCr_2O_7$ is obtained by dissolving barium chromate in hot concentrated chromic acid. On cooling, red crystals of the composition $BaCr_2O_7,2H_2O$ are deposited, which lose their water at 100°, and are decomposed by water into the normal chromate and chromic anhydride (Preis and Rayman, Ber. 13, 340).

Barium manganate $BaMnO_4$ is formed when manganese dioxide is heated with barium carbonate or nitrate as an emerald-green powder consisting of microscopic four-sided prisms or six-sided plates, insoluble in water but decomposed by acids. This salt is now used in place of the poisonous Scheele's green.

Barium permanganate $BaMn_2O_8$ is prepared

by passing carbonic acid gas through water containing barium manganate in suspension; after filtering off the barium carbonate the red solution is rapidly evaporated. Or it may be obtained by the action of barium chloride on silver permanganate.

Or potassium permanganate may be decomposed by slight excess of hydrofluosilicic acid, the mixture kept cool, and, after separation of the precipitated potassium silicofluoride, the supernatant solution decanted and saturated in the cold with barium hydroxide. After separation of the insoluble barium silicofluoride, the solution is evaporated until the barium permanganate separates out on cooling (Rousseau and Bruneau, Compt. rend. 98, 229).

It forms large orthorhombic octahedra, deep-red and almost black, with a violet reflection.

It is used for the preparation of permanganic acid and of the ammonium salt.

Rousseau and Saglier (Compt. rend. 99, 139) find that on heating two grams of barium manganate with ten grams of barium chloride for four hours to 1500°, and extracting with water and dilute acid, a residue of small opaque bluish-black crystals of *barium manganite* $BaMnO_3$ remains; sp.gr. 5·85; readily soluble in hydrochloric acid with evolution of chlorine. The manganite is also formed when mixtures of manganese chloride and barium oxychloride are heated below 1000° or above 1100°. Between these temperatures the product is barium dimanganite $BaO{\cdot}2MnO_2$, which crystallises in brilliant black lamellæ. At 1500° the manganite is reconverted to manganate.

Barium phosphide Ba_3P_2. When vapour of phosphorus is passed over red-hot baryta, a brownish-red mixture of barium phosphide and phosphate is obtained commonly known as 'phosphuret of baryta.' It is decomposed by water, forming a solution of hypophosphite of barium and evolving a mixture of free hydrogen and spontaneously inflammable phosphoretted hydrogen.

Jaboin (Compt. rend. 129, 762) prepared the phosphide by heating 100 parts of barium phosphate with 16 parts of lamp black in an electric furnace. The product so obtained has a crystalline structure. It decomposes water, yielding PH_3 and $Ba(OH)_2$.

Barium monometaphosphate is obtained as a white powder by evaporating a solution of barium carbonate in excess of metaphosphoric acid and heating the residue to 316°. Its formula is not known with certainty.

Barium dimetaphosphate $Ba(PO_3)_2{,}2H_2O$ is formed as a crystalline sparingly soluble precipitate when barium chloride is added to a solution of the corresponding ammonium or sodium salt.

Barium trimetaphosphate $Ba_3P_6O_{18}{,}6H_2O$, apparently a polymeric form of the last salt, is produced when a solution of 1 part of the corresponding sodium salt in 10 to 15 parts of water is mixed with a nearly saturated solution of 3 parts barium chloride. On standing, the salt separates in monoclinic prisms, which give off two-thirds of their water at 100°, and the rest at a higher temperature.

Barium hexametaphosphate is obtained as a gelatinous precipitate by precipitating the corresponding sodium salt with barium chloride.

Monobarium orthophosphate $BaH_4(PO_4)_2$ is prepared by evaporating a solution of the di- or tri-barium salt in aqueous phosphoric acid. It forms colourless crystals—triclinic according to Erlenmeyer, with acid reaction; soluble without decomposition in a small quantity of water, but decomposed by excess of water into free phosphoric acid and the neutral salt.

Joly (Compt. rend. 98, 1274) states that as the total weight of salt brought in contact with the same quantity of water increases in arithmetical progression, the weight which is dissolved without decomposition decreases in geometrical progression; but as soon as half the original salt has been decomposed a diacid salt is formed $BaO{\cdot}2P_2O_5+xH_2O$, the proportion of which increases as the acidity of the liquid increases, and eventually exists alone in solution.

Dibarium orthophosphate $Ba_2H_2(PO_4)_2$ or $BaHPO_4$ is obtained as a white, scaly, crystalline precipitate when hydrogen disodium phosphate is added to a neutral solution of a barium salt. It is soluble in 20,570 parts of water at 20°, somewhat more soluble in water containing barium or sodium chloride or ammoniacal salts. From the solution in nitric or hydrochloric acid excess of ammonia precipitates the tribarium salt or a salt intermediate between the two. Thus, according to Wackenroder, a solution of $BaHPO_4$ in nitric acid yields, on addition of ammonia, a precipitate of barium phosphato-nitrate $4BaHPO_4{\cdot}Ba(NO_3)_2$, which leaves, on heating, a mixture of di- and tri-barium phosphates.

By precipitating a solution of dibarium phosphate with alcohol, a salt intermediate between the mono- and di-salts is obtained:

$$BaH_4(PO_4)_2{\cdot}2BaHPO_4{,}3H_2O.$$

If a mixture of potassium silicate and baryta water is boiled, and afterwards mixed with a solution of potassium silicate containing a quantity of potassium phosphate, on cooling, cubical crystals of the composition $BaKPO_4{,}10H_2O$ separate out. $BaNaPO_4{,}10H_2O$ was similarly obtained in regular tetrahedrons (De Schulten, Compt. rend. 96, 706).

Tribarium orthophosphate, or neutral phosphate of barium, $Ba_3(PO_4)_2{\cdot}H_2O$ is prepared by adding hydrogen disodium phosphate to a solution of barium chloride rendered strongly alkaline by ammonia, and separates as a heavy granular powder. It parts with a portion only of its water at 200°.

If a saturated solution of tribarium phosphate in hydrochloric acid is evaporated, on cooling, crystals of barium chloride are deposited, more and more monobarium phosphate being left in solution, and if more hydrochloric acid is added, all the barium may be crystallised out as barium chloride, and pure phosphoric acid remains.

If the solution of tribarium phosphate in hydrochloric acid is boiled, shining needles form in the liquid, and on adding sufficient water to redissolve them, well-defined crystals of a phosphato-chloride $4BaH_4(PO_4)_2{\cdot}BaCl_2$ are deposited on standing (Erlenmeyer, J. 1857, 147).

According to Ludwig, a solution of dibarium phosphate in hydrochloric acid also yields, on addition of ammonia, a phosphato-chloride containing $3Ba_5H_2P_4O_{16}{\cdot}BaCl_2{\cdot}3H_2O$.

A salt intermediate between the di- and tri-phosphates, containing $Ba_3(PO_4)_2{\cdot}2BaHPO_4$ or

$Ba_5H_2P_4O_{16}$, is formed when a solution of the dibarium phosphate in hydrochloric acid is mixed with a quantity of ammonia just sufficient to precipitate it.

Barium pyrophosphate $Ba_2P_2O_7$. Pyrophosphoric acid does not precipitate barium salts, but with baryta water gives a precipitate of barium pyrophosphate. Barium salts, however, give with sodium pyrophosphate a white amorphous precipitate of barium pyrophosphate, soluble in aqueous pyrophosphoric and sulphurous acids; more soluble in hydrochloric or nitric acid, but not perceptibly soluble in water containing ammonium chloride or in acetic acid.

Monobarium arsenate $BaH_4(AsO_4)_2$ is obtained by adding baryta water to aqueous arsenic acid until a precipitate begins to form, or by dissolving the dibarium salt in aqueous arsenic acid and leaving the solution to crystallise.

Dibarium arsenate

$$2BaHAsO_4,H_2O \text{ or } BaHAsO_4,H_2O$$

according to Berzelius, is obtained when a solution of the disodium salt is added to excess of barium chloride. It gives up its water at a red heat, and in contact with water is decomposed into the tribarium salt, which is precipitated, and the monobarium salt, which dissolves.

Tribarium arsenate $Ba_3(AsO_4)_2$ is obtained as a white sparingly soluble powder by precipitating aqueous arsenic acid with baryta water, or better, by gradually dropping trisodium arsenate into barium chloride,

Barium silicate. Solutions of baryta, when kept in glass bottles for any length of time, deposit transparent rhombic crystals of the composition $BaSiO_3,7H_2O$. These crystals lose their water a little above 100°, and become turquoise-blue: they are decomposed by boiling water (Le Chatelier, Compt. rend. 92, 931); Cossa and Lavalle (Zeitsch. f. Chem. 11, 399).

According to Le Chatelier, they may be readily obtained in a few days, by suspending calcined silica in baryta water, when the sides become covered with crystals.

Barium titanate. When equivalent quantities of titanic anhydride and barium carbonate are fused at a bright red heat for an hour with excess of barium chloride, and the product extracted with very dilute hydrochloric acid, a residue of yellow microscopic crystals resembling cubes and octahedra of the composition

$$2BaO\cdot3TiO_2$$

and of sp.gr. 5·91 remains undissolved. These crystals are found on examination by polarised light to consist of aggregations of rhombic lamellæ.

Reactions of the compounds of barium. When heated on a thin platinum wire in the inner blowpipe flame, or when brought into any non-luminous flame, barium compounds impart a yellowish-green colour to the outer flame. When viewed through the spectroscope two green lines Baα and Baβ come out most intensely; Baγ, though not so marked, is also a characteristic line. Besides these, there are numerous lines in the red and yellow and one broad indistinct line in the blue, close to Fraunhofer's F. Bunsen found that $\frac{1}{1000}$ of a milligram of barium salt may be detected spectroscopically. Silicates of barium give this reaction on moistening with strong hydrochloric acid.

The hydrate, sulphide, chloride, bromide, iodide, nitrate, and many organic salts of barium are soluble in water, and all are poisonous. The majority of the remaining salts are soluble in hydrochloric and nitric acids, whilst the sulphate and silicofluoride are insoluble in all acids.

Alkaline carbonates precipitate white barium carbonate, soluble in most acids, hence ammonium carbonate is used to precipitate it (along with the carbonates of strontium and calcium) in qualitative analysis.

Potassium and sodium hydroxides, free from carbonates and sulphates, give a voluminous precipitate of barium hydroxide $Ba(OH)_2$ with concentrated solutions soluble in more water. Ammonia gives no precipitate.

Sulphuric acid, as well as all soluble sulphates, throws down barium sulphate from all solutions of barium salts. Pickering (Chem. News, 46, 223) states that the smallest quantity of barium which can be detected is 1 part in 833,000 parts of water. The presence of an alkaline citrate greatly interferes with the precipitation. Strontium sulphate (which is more soluble) forms a delicate test for barium.

Phosphate, arsenate, borate, and iodate of sodium also give precipitates soluble in acids.

Ammonium oxalate gives, from moderately dilute solutions, a white pulverulent precipitate of barium oxalate.

Potassium chromate precipitates bright lemon-yellow barium chromate, soluble in nitric, hydrochloric, or chromic acid.

Hydrofluosilicic acid gives a colourless crystalline precipitate of barium silicofluoride; this reaction will detect 1 part of the chloride in 3800 parts water. The precipitate is nearly insoluble in nitric and hydrochloric acids, more insoluble in alcohol.

Barium is readily distinguished from lead (which also forms a sulphate insoluble in water) by the fact that sulphuretted hydrogen gives a black precipitate of lead sulphide with soluble lead salts.

Soluble barium salts are at once distinguished from those of strontium and calcium by the fact that they are immediately precipitated by a solution of calcium sulphate, which only gives a precipitate with strontium salts on standing. The hydrofluosilicic acid reaction is also of use in separating barium from the other two metals. Barium chloride is insoluble in alcohol, whilst the chlorides of strontium and calcium are soluble, and the nitrates of barium and strontium are insoluble, in alcohol, whilst calcium nitrate is soluble. From these facts a scheme of separation is readily derived, the precipitated carbonates of barium, strontium, and calcium being converted into chlorides, and the chlorides of strontium and calcium dissolved out by alcohol, leaving a residue of chloride of barium. The strontium and calcium may then be separated by converting their reprecipitated carbonates to nitrates and dissolving out the calcium nitrate (*v.* ANALYSIS).

Estimation of barium. When no other alkaline metal is present, barium may be estimated as sulphate. A solution of the chlorides slightly acidified with hydrochloric acid is best. Sulphuric acid is added cautiously to the hot solution in slight excess. The precipitate is allowed to settle in a warm place for some hours before filtering.

In its organic salts barium may be estimated as carbonate by heating in a platinum crucible and subsequent moistening of the residue with a concentrated solution of ammonium carbonate, evaporation, gentle ignition, and weighing.

Where strontium and calcium are present, after the separation of the other elements, the alkaline earths are precipitated by ammonia and ammonium carbonate. This precipitate is then dissolved in acetic acid, and the barium twice precipitated as chromate, in which form it may be weighed or dissolved in hydrochloric acid, then precipitated, and weighed as sulphate.

G. S. B.

BARK BREAD. A kind of bread which was formerly made by the peasants in various parts of Norway from the inner bark of *Pinus sylvestris* (Linn.).

BARKLYITE *v.* CORUNDUM.

BARLEY. Two species are in common cultivation—*Hordeum distichum*, two-rowed, and *H. vulgare*, six-rowed. Many varieties are known, differing in size and shape of ear and grain. The two-rowed varieties are chiefly grown as spring-sown crops, while the six-rowed varieties are often sown in the autumn.

The grain resembles in composition that of other cereals, but contains less gluten than wheat; moreover, the gluten of barley is not so tenacious as that of wheat; consequently, barley meal does not yield a satisfactory bread.

Barley is chiefly grown for cattle-feeding and for malt production. For the latter purpose, a grain containing but little nitrogenous matter is preferred, so that too lavish nitrogenous manuring must be avoided in the production of malting barley.

The following are analyses of typical average barley as given by 1, Warington; 2–5, Kellner (German); 6, Wiley (of American barley).

The table represents the composition of barley expressed in the usual manner. The item 'nitrogenous substances' is simply the total nitrogen $\times 6{\cdot}25$. Of the total nitrogen, a small portion—probably about $\frac{1}{100}$—is present in non-albuminoid form.

	1 English	2 Medium	3 Large gr'nd	4 Flat gr'nd	5 Feeding	6 American
Water . .	14·3	14·3	14·3	14·3	14·3	10·85
Nitrogenous substances	10·6 [1]	9·4	8·7	10·2	12·0	11·00
Fat . . .	2·1	2·1	1·8	2·5	2·4	2·25
Soluble carbohydrates .	66·0	67·8	70·2	63·7	63·7	69·55
Fibre . . .	4·5	3·9	2·7	6·5	5·0	3·85
Ash . . .	2·5	2·5	2·3	2·8	2·6	2·50

According to Osborne (18th Ann. Rep. Conn. Expt. St.), the proteids in barley are: (1) Soluble: leucosine 0·30 p.c., hordein 4·0 p.c., edestine and proteose 1·95 p.c.; (2) insoluble proteids 4·50 p.c. The soluble proteids just mentioned contain an average of 17·6 p.c. of nitrogen, so that the factor to convert nitrogen into proteids in barley should be much less than 6·25, probably about 5·7. Consequently, the amount of proteids in barley should be about 1 p.c. less and that of carbohydrates (since they are determined by difference) 1 p.c. more than the values given in the tables.

Under the heading 'soluble carbohydrates' are included: pentosans 6·5 p.c. (Bull. 13, U.S. Dept. of Agric. 1898); cane sugar 0·8–1·6 p.c. (O'Sullivan, J. Chem. Soc. 1886, 49, 58); 1·3 p.c. (Banister, Chem. News, 1885, 298); 0·2 p.c. (Bull. 13, *l.c.*); small quantities of reducing sugars (O'Sullivan); dextrine and raffinose (O'Sullivan). The remainder is chiefly made up of starch and cellulose, though gum 2·8 p.c. (Muntz, Compt. rend. 102, 681) and amylan 2–4 p.c. (O'Sullivan, J. Chem. Soc. 41, 24) have also been found.

Barley contains diastase even before germination (when its amount is enormously increased). Brown and Morris (J. Chem. Soc. 1890, 505) recognise two kinds of diastase—of secretion, as formed in germination, which rapidly corrodes starch granules, and of displacement—present in the ungerminated grain—which slowly diminishes the volume of starch granules without visibly corroding them.

The ash of barley, neglecting the CO_2, has the average composition:

—	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	Cl	SiO_2
[1] Mean, 28 American samples	24·15	6·42	2·44	8·23	0·33	35·47	0 22	0·56	22·30
[1] „ 19 Canadian „	26·76	9·36	4·27	7·87	0·35	24·63	0·71	0·47	20·69
„ Wolff's analyses .	20·15	2·35	2·60	8·62	0·97	34·68	1·69	0·93	27·54

For a full yield of barley the soil must be well supplied with plant food, including combined nitrogen, but such a crop, though excellent from the farmer's point of view and valuable for feeding purposes, is rarely suited to the maltster's requirement. Good malting barley should be as rich as possible in starch and low in albuminoids. Between 8 and 9 p.c. of nitrogenous matter is usually regarded as the most desirable proportion in malting barley. If grown in hot, dry countries, *e.g.* Southern Russia, it is usually richer in nitrogen. The best malting barleys are grown on light soils not too rich in nitrogen, and in temperate climates (*v.* BREWING).

[1] Composite samples from the World's Columbian Exposition (Wiley, Bull. 13, U.S. Dept. of Agric.).

Owing to the injurious effect of too lavish a supply of nitrogen upon the malting properties of barley, it is by many considered best to take the barley crop after wheat, rather than after roots, though the latter procedure is often adopted in Ireland.

Pearl barley is barley deprived of its husk. American analyses give as its average composition: Water, 10·8 p.c.; protein, 9·3 p.c.; fat, 1·0 p.c.; carbohydrates, 77·6 p.c.; ash, 1·3 p.c.

According to Wolff's analyses, the ash of the barley kernel amounts to 2·13 p.c., and 100 parts of the ash contain:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2
28·5	1·8	3·1	12·0	1·9	47·1	2·9	3·6

[1] Of which 10·2 p.c. are albuminoids.

Barley straw is much more affected in composition than the grain by the richness or poverty of the soil, and by the conditions under which it is grown. If the ripening of the grain has been fully completed, the straw is robbed of its nitrogenous matter and phosphates to a much greater extent than when the seed has not been fully matured. Thus the straw of a crop cut before it is fully ripe possesses much higher feeding value than usual.

According to Kellner, the following represents the average composition of barley straw:—

	Water	Protein	Ether extract	Soluble carbohydrates	Fibre	Ash
Summer barley	14·3	3·5	1·4	35·9	39·5	5·4
Winter barley	14·3	3·2	1·4	33·5	42·0	5·6

The ash of barley straw (Wolff) contains:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
23·3	3·5	7·2	2·6	1·1	4·2	3·9	51·0	3·2

Barley straw consists largely of cellulose, and pentosans and lignose. The amount of pentosans has been estimated at about 25 p.c. The 'crude protein' given in the above table is probably nearly all true albuminoids, since direct experiments showed about 91 p.c. of the total nitrogen to be present as albuminoids. The lowest portions of the stems are least nutritious, while the uppermost leaves and top of the stem are the most digestible and richest in protein.

When barley precedes clover, as is often the case in England, the barley straw is enriched by including a portion of young clover plants. Under such circumstances, the product is of much higher feeding value, and contains more protein (up to 6 or 7 p.c.), and soluble carbohydrates (38 or 39 p.c.), and less crude fibre.

H. I.

BARUS CAMPHOR *v.* CAMPHORS.

BARUTIN. Trade name for the double salt of theobromine barium and sodium salicylate; a white amorphous powder of sweetish taste and alkaline reaction, sparingly soluble in water. Used in the treatment of renal disease. *V.* SYNTHETIC DRUGS.

BARWOOD *v.* SANDERSWOOD.

BARYTA, GREEN, *v.* BARIUM.

BARYTES. Barite, or heavy-spar (from *βάρυς*, heavy); a common mineral consisting of barium sulphate ($BaSO_4$), and crystallising in the orthorhombic system. The name barytes is, however, sometimes loosely, but incorrectly, applied to include both this species and the mineral witherite ($BaCO_3$, *q.v.*), or these are occasionally referred to as 'sulphate of barytes' and 'carbonate of barytes' respectively. The reason for this confusion is that the two minerals are often mined together, although they are not always put to the same uses.

Barytes is frequently to be found as well-developed crystals, which vary considerably in their appearance and habit. They possess a perfect cleavage parallel to the base, and perpendicular to this are two prismatic cleavages parallel to the faces of the primitive rhombic prism, and thus inclined to one another at an angle of 78° 22½'. With these three directions of perfect cleavage, massive barytes sometimes presents a certain resemblance to calcite, and its hardness is also about the same (H.=3). The angles between the cleavages are, however, different; and, further, barytes may be readily distinguished from calcite by its heaviness (sp.gr. 4·5), and from both calcite and witherite by not effervescing with acid. The massive material is often white and opaque; but crystals are sometimes transparent and colourless, or with brownish, greenish, or bluish shades of colour.

Barytes is usually met with in veins, often in association with ores of lead. Some of the old lead-mines of the north of England and Shropshire are now being reworked for barytes. A remarkable vein of barytes, consisting of pure white massive material with a thickness varying from a few inches to 16 feet, is extensively worked in the coal-measures at New Brancepeth Colliery, near Durham (L. J. Spencer, Mineralog. Mag. 1910, xv. 302). Beautiful crystallised specimens are abundant in the hæmatite-mines of west Cumberland, but, owing to the brown or yellow colour of this material, it is of no commercial value.

Barytes is mainly used in the manufacture of paints, not only of white paint, but as an inert body in coloured paints. It is often suggested that barytes is used for adulterating various articles. Barium sulphide and carbonate are also prepared from barytes by roasting it with coal, and from the product, barium chloride is largely obtained. In preparing the crude barytes for the market, it is coarsely crushed and hand-picked; or when mixed with rock and dirt, these are separated by agitation (jigging) in water. Coloured impurities are sometimes extracted by steam-boiling with sulphuric acid. The purified material is kiln-dried and reduced to very fine white powder in a ball-mill provided with screens, or between millstones. The barytes flour so prepared still consists of minute crystalline (cleavage) particles, and it is this that gives the 'tooth' or adhesive properties to the coarser barytes paints. The finer qualities are prepared from precipitated barium sulphate; and this is also used for dressing cloth and leather, and for producing the smooth coating on 'art' papers.

L. J. S.

BARYTIC WHITE or **PERMANENT WHITE** or **BLANC FIXE** *v.* BARIUM; also PIGMENTS.

BARYTO-CÆLESTITE *v.* BARIUM.

BASE OILS *v.* OILS and FATS.

BASIC BESSEMER STEEL *v.* IRON.

BASILICON. *Resin cerate.* A mixture of oil, wax, and resin.

BASIL OIL *v.* OILS, ESSENTIAL.

BASLE BLUE *v.* AZINES.

BASSIA or MAHWA FLOWERS. The flowers of *B. (illipé) latifolia* (Roxb.) or Mahwa, a tree growing to the height of 60 feet, very abundant in Central India, are very succulent, and fall from the tree in large quantities every night, a single tree affording from 200 to 400 lbs. of flowers in a season, which lasts during March and April. They are used as an article of food, both cooked and raw. By fermentation and distillation they yield upwards of 6 gallons of proof spirit per cwt. It is of superior quality, and when the operations have been carefully performed, is very much like good Irish whisky, having a strong smoky and rather fœtid flavour, which disappears with age.

They have also been used as a cattle food with success. It is said that the flesh of pigs and other animals is much improved, acquiring a delicate flavour.

The dried flowers have been recommended as a source of sugar. Negri found in them 57·9 p.c. of glucose, yielding 26·74 p.c. of alcohol on distillation (Rev. Chim. Med. Pharm. 2, 384; *cf.* von Lippmann, Ber. 1902, 35, 1448).

BASSIA OILS. Under this name are comprised a number of oils belonging to the genus *Bassia*. The most important oils (or fats) derived from *Bassia* species are: Mowrah Seed Oil, Illipé Butter, Shea Butter, Njave Oil, and Phulwara Butter.

Mowrah Seed Oil is the fat obtained from the seeds of *Bassia latifolia* (Roxb.) (*Illipé latifolia*, Roxb. or Engler; *Bassia villosa*, Wall.), a tree widely distributed in the northern provinces of India, and especially in Bengal. The tree is frequently cultivated in East India, and forms small plantations; but even under the incentive of modern demand for a solid fat, the cultivation of the Mowrah Seed tree for the production of fat is not likely to be taken in hand in the near future. The tree gradually disappears towards Calcutta, and is only sparingly met with in the Madras presidency, where its place is taken by *Bassia longifolia* (*see* below).

The kernels are 1–2 cm. long, and are enclosed in a light-brown shiny husk. The seeds are very similar in appearance to those of *Bassia longifolia*, with which they are frequently confounded, much as the fat obtained from both species is frequently confounded in commerce. This is partly due to the fact that the two kinds of fats are mixed together when exported to Europe, a practice which is greatly favoured by the fact that both species are known to the natives under such similarly sounding names as Illipi, Elupa, Katillipi.

The kernels dried at 100° contain, according to Valenta:

Fat extracted (by petroleum ether)	51·14
„ soluble in absolute alcohol	7·83
Tannin	2·12
Bitter principle, soluble in water	0·60
Starch	0·07
Vegetable mucilage	1·65
Albuminous substances soluble in water	3·60
Extractive substances soluble in water	15·59
Insoluble proteids	4·40
Total ash	2·71
Fibre and loss	10·29

In its fresh state the fat is yellow; on exposure to the air the colouring matter is bleached. The oil can also be bleached chemically, as has been done by the author, on a large scale.

The fat has the sp.gr. of 0·9175 at 15°, melts at about 25·3°–30°, and solidifies at 18·5°–22°.

The fat has a bitter aromatic taste and a peculiar odour. The iodine value of the fat is 50, thus indicating a considerable amount of oleic acid. The chief constituent of the solid fatty acid is palmitic acid; arachidic acid is absent; stearic acid has been found to occur in specimens examined recently in the author's laboratory by Menon, to the extent of from 13 to 25 p.c. The saponification value of the commercial fats is slightly lower than that of fats having the constitution due to the fatty acids named, owing to a somewhat high proportion of unsaponifiable matter, viz. 2·34 p.c. The fat is prepared in India in a crude manner, and the cakes are used as manure. Owing to a bitter principle (saponin) contained in the cakes, they are unfit as food for cattle. Nevertheless, the cake is frequently added as an adulterant to the so-called 'native linseed cake,' which, under this misleading name, has latterly found extensive sales on the Continent. The seeds and the oil have recently become an important article of commerce. They are imported to Europe in irregular quantities, and are chiefly used in the soap and candle industries. Endeavours have also been made to convert the fat into an edible fat. In India, Mowrah seed oil is largely used as an edible fat under the name 'Dolia oil,' and as a medicinal oil in the treatment of skin diseases under the name 'Me oil.'

Illipé Butter is obtained from the seeds of *Bassia longifolia* (Linn.), a tree indigenous to the southern part of India; a variety of this *Bassia* species is known as *Illipé malabarica* (König), in the Western Ghats from Kanara to Travancore and the Anamalais, where the tree is found at an altitude of about 4000 feet. The seeds bear a close resemblance to those of *B. latifolia*, but are mostly 3–4 cm. long, and less rounded than the seeds of *B. latifolia*. The average weight of one seed is 1·4 grms. The kernels form 75 p.c. of the seeds, and contain 50–55 p.c. of a white to light-yellow coloured fat. The fat closely resembles Mowrah seed oil, but differs from it by its lower solidifying and melting points; in correspondence therewith the iodine value of the fat is 58–64, *i.e.* higher than that of *B. latifolia*. The fat contains from 12 to 20 p.c. of stearic acid; arachidic acid is absent (Menon).

Illipé seeds are imported into France and England (mostly admixed with Mowrah seeds), where the fat is expressed for use in candle-making. The proposal to employ the fat as a chocolate fat appears to be due to the confounding of true Illipé seeds with seeds from the Malayan States, erroneously described in the French market as 'Illipé nuts.'

Shea Butter is the fat obtained from the seeds of *Bassia Parkii*, De C. (Hassk.), *Butyrospermum Parkii*, [G. Don] (Kotschy), a tree belonging to the *Sapotaceæ*. The tree was first described by Mungo Park, who found it in the kingdom of Bambara. Hence the fat was known as Bambara fat and also Bambooi fat. Other native names are Galam Butter, Bambuk Butter, and, in French West Africa, Karité Oil. The Shea Butter tree, or Karité tree, resembles in appearance the American oak, grows to a height of about 40 feet, and occurs in enormous quantities on the West Coast of Africa, and through the centre of Africa in the French and English Soudan. It is especially abundant in the middle basin of the Niger, and is as characteristic of the region of the middle Niger as is the palm tree of the lower reaches of the rivers and of the coast line. The Shea nut has the size and shape of an ordinary plum; the outer shell of some specimens is covered with fine fibres, whereas the shell of nuts coming from the middle Niger district has a polished surface. Owing to the wide distribution of the tree, the different specimens of nuts and fats exported to Europe show characteristic differences. A special variety appears to be represented by the specimen known as *Bassia niloticum* (Kot-

schy et Chevalier). (For a table stating the different yields of fat from different specimens, and some of their characteristics, *see* Lewkowitsch, Chemical Technology, &c., ii. 433.) The natives extract the fat by pounding the kernels and boiling the paste with water. The fat rises to the surface and is skimmed off into large calabashes, in which it is carried to the river for shipment. Since little care is taken in the preparation of the exported oil, most of the shea butter that came until recently to Europe had a dark-grey colour, which was considered to be characteristic of shea butter. The fat used by the natives for their own purposes is, however, prepared in a more careful manner, made into cakes and wrapped round with leaves, so that the fat may keep. This fat is of a white colour, and keeps well for several months.

Shea butter plays a very important part in the economy of the natives as an edible fat, and also as a burning oil, and for cosmetic purposes. Attempts have been frequently made to ship the fat and the nuts in bulk to Europe. Owing partly to the careless preparation, and partly to a resinous substance dissolved by the fat, shea butter contains considerable amounts of unsaponifiable matter which imparts to the fat an indiarubber-like taste. This large amount of unsaponifiable matter precludes the employment of the fat for soap-making purposes; it is, however, used in candle-making.

The specific gravity of the fat is 0·9177; its melting-point varies from 25° to 28°. Owing to the considerable amount of unsaponifiable matter, the saponification value varies from 171 to 192. The iodine value varies from 56 to 63, so that the proportion of oleic acid in the fat may be taken to reach about 60 p.c. The author found in a number of shea butters from 33 to 37 p.c. of stearic acid. The remainder of the fatty acid appears to consist of lauric acid (Southcombe, J. Soc. Chem. Ind. 1909, 499).

Njave Oil, *Njave Butter, Nari Oil, Noumgou Oil, Adjab Oil*, is the oil obtained from the seeds of *Mimusops Njave* (De Lanessan), *syn. Bassia Djave* (De Lanessan); *Bassia toxisperma* (Raoul) *Tieghemella africana* (Pierre); *Baillonella toxisperma* (Pierre); *Baillonella Djave* (Pierre); *Tieghemella Jollyana* (Pierre), a tree belonging to the family of the *Sapotaceæ*. The wood of this tree is known in commerce as 'Cameroon mahogany.' The tree is indigenous to West Africa, the Cameroons, Gaboon, Nigeria, and furnishes, like most trees belonging to the *Sapotaceæ*, guttapercha. The fruits are known in commerce as 'Mahogany nuts'; in the Gold Coast Colony they are known as 'Abeku' and 'Bako' nuts. The weight of the nuts varies between 10 and 21·6 grams., one-third of which is made up by the shell. The kernels contain 43–64 p.c. of a white fat, which the natives (the *Jaundes* and the *Ngumbas*) prepare by drying the seeds over fire and breaking the shell with stones. The kernels are then pounded in a mortar or comminuted by rubbing between stones. The mass is next boiled out with water, the fat is skimmed off by hand, and freed from the bulk of water by squeezing between the hands, and then subjecting it to a somewhat stronger pressure in baskets, by heaping stones on the mass. By this process an extremely poisonous saponin, contained in the fresh seeds, is completely removed, so that the fat can be used for edible purposes. In case the seeds should be expressed on a large scale the press cakes would retain the poisonous substance, and hence be valueless as a feeding cake (Der Tropenpflanzer, 1910, 29), unless the saponin be removed completely by boiling out with water. But even if this process were feasible, a considerable amount of nutritive substances would be removed thereby. The economic prospects of the seeds are, therefore, still doubtful; nevertheless, the exports from the German Cameroons have increased from 3 tons in 1906 to 183 tons in 1908.

Phulwara Butter is the fat expressed from the kernels of *Bassia* (*Illipé*) *butyracea* (Roxb.), the 'Indian butter tree,' which is indigenous to the Himalayas. The seeds are smaller and thinner than those of *B. latifolia* and *longifolia*. The average weight of one seed is one gram. The kernels form 67·5 p.c. of the total seed; they contain 50–65 p.c. of a white fat, having the consistence of lard. Phulwara Butter is one of the most important foodstuffs amongst the natives of the North-West Provinces, on account of its pleasant odour and agreeable taste. The butter is also highly valued by the natives as an ointment when properly perfumed. The melting-point of the fat is 39°, and its iodine value 42°. Stearic acid is absent (Menon).

Less-known Bassia Oils are: *Payena Oil* or *Kansive Oil*, from *Payena oleifera* (Chemical Technology and Analysis of Oils, Fats, and Waxes, ii. 800), and *Katio Oil*, from an undetermined species of *Bassia* (Brooks, Analyst, 1909, 207). J. L.

BASSWOOD OIL. An oil from *Tilia americana*, resembling cotton-seed oil, and consisting of glycerides rich in butyric acid (Wiechmann, Amer. Chem. J. 1895, 17, 305).

BAST FIBRES. Elongated narrow plant-cells that form strengthening tissue in stems and leaves, especially in connection with the fibro-vascular bundles, but not belonging to the wood. The raw material, bast or bast-like fibre, used for textile purposes or for the manufacture of paper, ropes, and the like, is of varied nature and source, but is always characterised by the abundance in it of bast fibres. It may be composed of a number of fibro-vascular bundles, or one such bundle (*e.g.* coco-nut fibre), or part of fibro-vascular bundle (*e.g.* fibre from leaves of monocotyledons), or merely a bundle of true bast fibres (from the fibro-vascular bundles or bark of dicotyledonous stems).

A typical bast fibre has a thick wall, with slit-like oblique pits, and a relatively small lumen. The ends usually taper to fine points, but may be blunt or even branched. The cell-wall varies in thickness in different species, from comparatively thin to extremely thick, and may vary in the same fibre, so that the lumen is alternately wider and narrower. When the wall is very thick the lumen is reduced to a line, and may be locally evanescent. There are similar differences in the width, length, and strength of the raw material and individual bast fibre. The colour varies from the usual whitish-grey or green or yellow, through yellow and brown to black.

The cell-wall is mainly composed of celluloses

and in certain species (flax, *Calotropis gigantea*, and others) is entirely soluble in ammoniacal cupric oxide, and gives the colour reactions for celluloses; but the bast fibres of certain other species (jute, hemp, esparto, and others) show lignification, and give corresponding colour reactions.

Bast fibres in commercial use are mainly obtained from comparatively few alliances and families of dicotyledons, and genera of monocotyledons, namely, Malvales (Malvaceæ), Tiliaceæ, Sterculiaceæ, Urticales (Moraceæ, Urticaceæ, Ulmaceæ), Leguminosæ, Linaceæ, Apocynaceæ, and Asclepiadaceæ, Boraginaceæ; *Agave* and *Fourcroya*, *Aloë*, *Bromelia*, *Sanseviera*, *Musa*, *Stipa*, *Pandanus*, and several palms (*See* articles on any of these, and JUTE and HEMP. For a full authoritative account of vegetable fibres, *see* Wiesner, Die Rohstoffe des Pflanzenreichs, 1903, Bd. ii. 167–463.)

BATATAS, or Sweet Potatoes, the tubers of *Ipsomœa batatas* or *Batata edulis*, a convolvulus-like plant, usually with purple flowers, growing freely in tropical and sub-tropical countries. The tubers are sometimes of great size—up to 12 lbs. or more in weight.

It can be propagated by cuttings or by the tubers, and, once established, often yields several crops in succession. An average crop is about 5 tons per acre. Light friable soils are most suitable.

Average composition of sweet potatoes and their vines:

	Water	Protein	Fat	Soluble carbohydrates	Fibre	Ash
Tubers .	71·1	1·5	0·4	24·7	1·3	1·0
Vines .	41·6	7·6	2·1	29·3	13·6	5·8

A more detailed analysis of the tubers as grown in Monte Video, is given by Sacc (Bied. Zentr. 1883, 337):

Water	Protein	Glucose	Mucilage	Pectic acid	Starch	Fibre	Ash
67·0 to 68·2	0·56 to 0·64	0·3 to 4·0	1·15 .	1·27	13 to 15	10 to 17·8	1·0

The sweet potatoes are largely used as food, and also in the manufacture of alcohol.

According to Stone (Ber. 1890, 23, 1406), they contain from 1·5 to 2·0 p.c. of cane sugar, and baking converts the starch into the soluble form and hydrolyses the cane sugar. The tops of sweet potatoes are greedily eaten by farm animals, but should be used with care, since they sometimes contain a poisonous cyanogetic glucoside. Amounts of hydrocyanic acid, varying from 0·014 to 0·019 p.c. of the green material, have been found. Sweet potato vines have often proved fatal to pigs in Queensland. H. I.

BATH BRICK. A brick made from deposits of silicious and calcareous earth at Bridgewater, Highbridge, and elsewhere, and used for polishing metals.

BATH-METAL. An alloy of copper and zinc, containing a larger proportion of copper than ordinary brass, viz. 83 p.c. copper to 17 p.c. zinc; sp.gr. 8·451; fracture crystalline, and colour yellowish-red.

BATIST. A material consisting of cotton impregnated with caoutchouc on one or both sides, largely used in the French army for compresses and antiseptic dressings.

BAUXITE. A clay-like aluminium hydroxide first noticed by P. Berthier in 1821 (*alumine hydratée des Beaux*), and named beauxite by A. Dufrénoy in 1847, and bauxite by H. Sainte-Claire Deville in 1861; this name being from the village Les Beaux, or Les Baux, near Arles, dep. Bouches-du-Rhône, in the south of France, where the material was found. This material came to be regarded as a mineral species with the composition $Al_2O_3,2H_2O$ or $Al(OH)_3$, corresponding with Al_2O_3, 73·9; and H_2O, 26·1 p.c.; that is, intermediate between the definite crystallised species diaspore (Al_2O_3,H_2O) and hydrargillite or gibbsite ($Al_2O_3,3H_2O$). It, however, varies widely in composition, owing to intermixture with quartz-sand, clay, and iron hydroxide, and it passes insensibly into clays, iron-ores, and laterite. The variations shown by different analyses are: Al_2O_3, 30·3–76·9; H_2O, 8·6–31·1; Fe_2O_3, 0·1–48·8; SiO_2, 1·1–41·5; TiO_2, 1·6–4·0 (from table of analyses quoted by G. P. Merrill, The Non-metallic Minerals, New York, 1904). (For other analyses of French bauxite, *see* H. Arsandaux, Compt. rend. 1909, 148, 936, 1115.)

The material never shows any indications of crystalline structure, being always compact or earthy, or often with a concretionary (pisolitic or oolitic) structure. In colour it ranges from white, through creamy and yellow, to brown and deep red. Under the microscope it shows only optically isotropic, flocculent grains. Bauxite is thus no doubt a mixture of colloidal aluminium hydroxides (for which the mineralogical name kliachite has been proposed by F. Cornu, 1909) with various iron hydroxides, clays, &c., and possibly also the crystalloids diaspore and hydrargillite; and it is thus rather of the nature of a rock than a simple mineral.

In its mode of occurrence, and no doubt also in its mode of origin, it also shows wide differences. The extensive deposits in the south of France have the form of beds interstratified with limestones of Cretaceous age, or of irregular pockets in the limestone. Those of Co. Antrim and of the Vogelsberg and Westerwald in Germany, are associated with laterite, and are interbedded with basaltic lava-flows. In Arkansas the bauxite deposits occur only in Tertiary areas in the neighbourhood of eruptive syenites, while in Alabama and Georgia they overlie ancient sedimentary rocks. The frequent presence of pisolitic structures in the material and its association with limestones, has led to the suggestion that bauxite has been deposited by hot springs containing aluminium salts in solution (probably aluminium sulphate from the decomposition of pyritous shales), where these have come into contact with limestone rocks. On the other hand, the material associated with laterite and basalt has, no doubt, been produced by the weathering under special conditions (the agency of bacteria has been suggested) of basalt or of other igneous and crystalline rocks. (For papers on the constitution of bauxite and laterite; *see e.g.* M. Bauer, Jahrb. Min. 1898, ii. 163; and T. H. Holland, Geol. Mag. 1903, 59.)

The alum-clay or bauxite mined in Co. Antrim is all sent to the aluminium works at Foyers and Kinlochleven in Scotland. In

France the present source of supply is mainly in dep. Var; and in America the production is confined to the states of Alabama, Georgia, and Arkansas. The French bauxite is roughly divided into three classes: (1) white bauxite, with 60 p.c. alumina, not more than 4 p.c. iron, and no silica,—this being used for the manufacture of aluminium salts and alum; (2) red bauxite, with 60 p.c. alumina and 3 p.c. silica,—used for the manufacture of aluminium; (3) a special kind of white bauxite, with 45 p.c. alumina, a trace of iron, and much silica,—used for making refractory bauxite bricks. The greater part of the material is used in the manufacture of aluminium, but in America large quantities are fused in the electric furnace to produce artificial corundum, which, under the name of *alundum*, is largely used as an abrasive agent. L. J. S.

BAYBERRY TALLOW *v.* WAXES.

BAY-LEAF OIL *v.* OILS, ESSENTIAL.

BAY-SALT *v.* SODIUM CHLORIDE.

BDELLIUM *v.* GUM RESINS.

BDELLIUM RESIN *v.* RESINS.

BEAN. The name given to many seeds which resemble in size and shape the ordinary kidney bean. Thus the seeds of coffee, cocoa, castor, &c., are often known as 'beans.' Usually, however, the term is restricted to seeds of various *leguminosæ*.

The most important species of beans are:

(1) Adzuki beans (*Phaseolus radiatus*).

(2) Field or horse beans, of which the broad bean is a variety (*Vicia faba*).

(3) French or kidney bean (*Phaseolus vulgaris*).

(4) Java or Lima bean (*Phaseolus lunatus*).

(5) Soy or Soja bean (*Glycine hispida* or *Soja hispida*).

(6) Velvet bean (*Mucuna utilis*).

(7) Carob or locust bean (*Ceratonia siliqua*).

In chemical composition beans are remarkable for the large proportion of albuminoid matter which they contain. They thus possess high nutritive value as foods.

In some cases the seed only is eaten, either green as in broad beans, or dried as in haricot beans, which are a variety of *Phaseolus vulgaris*. In others, *e.g.* in the kidney bean, the whole pod, in the unripe condition, is eaten; whilst in the case of the carob bean, the dried pod rather than the seeds is the valued product. The velvet bean is usually grown for its foliage, either for making into hay for cattle or for green manuring.

In the following table are given analyses of various beans, as far as possible of the products as they are usually consumed as food:—

—	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Water	13·6	87·3	11·1	68·5	14·4	10·0	16·0	9·3	19·7
Protein	23·1	2·2	15·9	7·1	23·9	33·2	17·2	13·3	5·5
Fat	2·3	0·4	1·8	0·7	1·6	17·5	2·2	2·6	0·8
Soluble carbohydrates	56·6	9·4	67·1	22·0	49·3	30·2	28·9	39·4	39·6
Crude fibre	3·9				7·5	4·4	29·5	27·6	7·8
Ash	3·5	0·7	4·1	1·7	3·2	4·7	6·2	7·8	2·5
Undetermined	—	—	—	—	—	—	—	—	24·1

(1) *Phaseolus vulgaris*, dried seeds, as used as haricot beans.

(2) *Phaseolus vulgaris*, green pods, as used as kidney beans.

(3) *Phaseolus lunatus*, dried.

(4) „ „ green.

(5) *Vicia faba*, dried.

(6) *Soja hispida*, dried seeds.

(7) „ „ hay.

(8) *Mucuna utilis*, hay.

(9) *Ceratonia siliqua*, whole pod.

The albuminoids of beans were thought to consist largely of legumin, or 'vegetable casein,' first obtained from them by Einhof in 1805, but Hoppe-Seyler has shown that the vegetable casein is produced by the action of the alkali used in extraction upon the globulins and albumins present in the seeds.

The proteids of *Phaseolus vulgaris* are chiefly phaseolin, a globulin containing 16·45 p.c. N and 0·5 p.c. S, and phaselin (Osborne, J. Amer. Chem. Soc. 1894, 16, 633). In *Phaseolus radiatus* are present phascolin and another globulin containing 16·31 p.c. N and 0·88 p.c. S (Osborne and Campbell, J. Amer. Chem. Soc. 1897, 19, 509). In *Vicia faba*, the same investigators found legumin, vicilin, legumelin, and a proteose (same Journal, 1898, 20, 393). In *Soja hispida* they found, as the chief proteid, a globulin resembling legumin, but containing twice as much sulphur, for which they propose the name glycinin. Legumelin, a trace of a proteose, and a globulin, probably identical with phaseolin, were also present (*l.c.* 20, 419).

According to Fleurent (Compt. rend. 1898, 126, 1374), bean flour contains 31 p.c. of nitrogenous matter, comprising legumin, 18·9 p.c.; vegetable albumin, 0·2 p.c.; glutenin, 9·5 p.c.; and gliadin, 2·4 p.c.; and has been used to add to wheaten flour, since the addition of 2 or 3 p.c. to the latter increases the ratio of glutenin to gliadin in the mixture, and thus in many cases improves the flour for bread making. The flour made from haricot beans contains starch as ovoid grains with distinct elongated or fissured hila, and square or rectangular cells containing prismatic crystals of calcium oxalate.

The fat of beans contains choline, cholesterol, and glycerides of valeric, oleic, and palmitic acids, but no stearic acid (Jacobson, Zeitsch. physiol. Chem. 1889, 13, 32). According to Kosutany (Landw. Versuchs-Stat. 1900, 54, 463), bean oil resembles olive oil in appearance, has a sp.gr. of 0·967, Reichert-Messel number 2·46, iodine number (Hübl.) 119·9, and contains much lecithin and sulphur. Staněk (Zeitsch. physiol. Chem. 1906, 48, 334) found both betaine and choline in horse beans.

Several varieties of beans contain a cyanogenetic glucoside. In *Phaseolus lunatus*, Dunstan

and Henry (Proc. Roy. Soc. 1903, 72, 285) found a glucoside which they named phaseolunatin $C_{10}H_{17}O_6N$, yielding dextrose, prussic acid, and acetone on hydrolysis. The wild plant contains it in much larger quantity than the cultivated one. From haricot beans Tatlock and Thomson (Analyst, 1906, 31, 249) obtained from 0·001–0·009 p.c. of hydrocyanic acid. Most of the cyanogen compound, and the whole of the enzyme which hydrolyses it, are destroyed by boiling.

The carob or locust bean is remarkable for the large amount of sugar (cane sugar 23 p.c., glucose 11 p.c.) contained in the pod, while the seed contains a carbohydrate, caroubin, a white, spongy, friable substance, of the same composition as cellulose (Effront, Compt. rend. 1897, 125, 38), which yields in contact with water a very syrupy liquid or jelly, 3 or 4 grams of the substance being sufficient to convert a litre of water into a thick syrup. Caroubin might be used with advantage in the preparation of nutrient media for bacteriological work.

It has been introduced under the name of 'tragasol' as a gum for sizing, colour printing and dyeing (J. Soc. Chem. Ind. 1894, 410, and 1896, 112).

Effront (Compt. rend. 1897, 125, 309) states that by hydrolysis, either by dilute acids or the enzyme caroubinase, present in the seeds, caroubin yields a sugar, which he calls caroubinose, resembling dextrose, but with lower rotatory power.

Van Ekenstein (Compt. rend. 1897, 125, 719), however, finds this sugar to be identical with *d*-mannose. So, too, Bourquelot and Herissey find that the action of dilute acid upon the carob seed yields a mixture of mannose and galactose so that caroubin apparently consists of mannans and galactans (Compt. rend. 1899, 129, 228 and 391). For analyses of commercial carobs *v.* Balland, J. Pharm. chim. 1904, 19, 569.

All species of beans, like other leguminosæ, serve as hosts for the tubercle-forming, nitrogen-fixing organisms (*Bacillus radicocola*), and thus, under suitable conditions, are independent of supplies of combined nitrogen in the soil. Beans are therefore sometimes used for enriching soils in combined nitrogen, being employed for green manuring, though the root *débris* of a crop of beans, even after the removal of the seed and haulms, often effects this object to a considerable extent. H. I.

BEAN OIL. *See* SOYA BEAN OIL.

BEBEERU BARK. The dried bark of *Nectandra Rodiæi* (Hook.), the greenheart tree, obtained from British Guiana, contains bebeerine or bebirine

$C_{18}H_{21}NO_3$, or $OH{\cdot}C_{16}H_{14}O(OMe)$: NMe,

to which its strong persistent bitter taste is due. Occasionally used as a tonic and anti-periodic.

Bebeerine is a tertiary amine, m.p. 214°, and forms crystalline salts. Is optically active: 1·6 p.c. sol. in alcohol, has a rotation $[\alpha]_D = -298°$ (Scholtz, Ber. 1896, 29, 2054).

BEECH NUT OIL *v.* OILS and FATS.

BEECH TAR. According to Fisher, 100 parts of beech wood yield on dry distillation 45 parts of acetic acid, 23 parts of charcoal, 4 of oil, and 28 of gas, consisting of 20 parts carbon dioxide, 7 of carbon monoxide, 0·5 of marsh gas, 0·05 of hydrogen, and 0·45 of water (Dingl. poly. J. 238, 55).

The tar contains phenol, cresol, phlorol, guaiacol, and creosol, the dimethyl ether of propyl pyrogallol, the dimethyl ether of pyrogallol, which on oxidation yield cœrulignone or cediret, pittacal, and picamar.

According to Gratzel (J. Pharm. [5] 6, 520), ferric chloride colours beech tar creosote a blue passing to brown.

(For a history of the investigations made upon wood tars, *v.* Schorlemmer, J. Soc. Chem. Ind. 4, 152, where also will be found a bibliography of the subject; *v.* also CREOSOTE, and WOOD, DESTRUCTIVE DISTILLATION OF.)

BEESWAX *v.* WAXES.

BEET-ROOT. The root of *Beta vulgaris* (Linn.). Many varieties are known, differing in colour, shape, and size. Mangel-wurzel, or mangold, as it is often called, is a variety (of which there are many sub-varieties), largely grown as winter food for cattle; garden beet-root, employed as salad or vegetable, is often understood when the term 'beet-root' is used. The most important variety, however, is the sugar beet, of which many sub-varieties are known. These have been obtained by careful selection with a view to obtaining the highest proportion of cane sugar.

The presence of sugar in the juice of beet-root was observed in 1747 by Marggraf, who suggested its extraction on a commercial scale. The early attempts, however, proved failures, as the process could not compete with the cane-sugar industry. This is not surprising when it is remembered that the beets then grown only yielded about 2 p.c. of sugar.

Careful selection of seed, and improved cultivation and methods of extraction, aided by a system of bounties by continental Governments, have resulted in beet sugar almost entirely replacing cane sugar in the principal markets of Europe (*v.* SUGAR).

Beet-root contains water, nitrogenous matters (including true albuminoids and the bases glutamine, betaine, and choline), pectins, sugars (of which cane sugar and raffinose are the chief), colouring matter of an unstable character (Formanek, J. pr. Chem. 1900, ii. 62, 310), and ash. It will be well to consider, in turn, the composition of average specimens of the three principal varieties of beet-root mentioned above.

(*a*) *Mangel-wurzel*, or *Mangolds*, called sometimes field beets. Many varieties, differing in colour, size, and shape, are in cultivation. They may be classified into long, tankard, and globe forms.

Mangolds grow best in deep, somewhat clayey soils, and in warm, fairly dry climates. They demand abundant supplies of plant food, and, under favourable conditions, yield very heavy crops, from 20 to 30 tons per acre being usually obtained. They are better as food for cattle and sheep after they have been stored for some weeks.

As in almost all root crops, large mangolds are distinctly more watery than small ones.

The following is the average composition of mangolds, according to (1) Warington, (2) Kellner:—

—	1		2		
	Large	Small	Large	Medium	Small
Water . .	89·0	87·0	89·5	88·0	86·5
Nitrogenous substances	1·2	1·0	1·3	1·2	1·1
Ether extract	0·1	0·1	0·1	0·1	0·1
Soluble carbohydrates	7·7	10·2	6·7	8·7	10·6
Crude fibre .	1·0	0·8	1·0	0·9	0·8
Ash . .	1·0	0·9	1·4	1·1	0·9
	100·0	100·0	100·0	100·0	100·0

The nitrogenous substances comprise real albuminoids, in proportion varying from 33 to 60 p.c. of the whole (being lowest in the large and highest in the small roots), and amides. Quite considerable quantities of nitrates are often present in the juice.

The soluble 'carbohydrates' consist chiefly of sugars, pectins, cellulose, and pentosans; starch is not present. The ash of mangolds, according to Wolff, contains:

K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	Cl	SiO_2
53·1	14·3	5·1	4·6	9·6	3·3	6·6	3·3

The unusually large proportion of chlorine is a noticeable feature. Beets, being descendants of a maritime plant, are found to be benefited by applications of common salt to the soil in which they are grown. Oxalic acid, to the extent of about 0·1 p.c., is present in beet-root.

(*b*) *Garden beet-root.* These are almost always red-fleshed. In composition they resemble the mangel-wurzel.

The average of 17 American analyses shows: Water, 87·6 p.c.; nitrogenous substances, 1·6 p.c.; fat, 0·1 p.c.; soluble carbohydrates and fibre, 9·6 p.c.; ash, 1·1 p.c.

(*c*) *Sugar beets.* Of these, many varieties have been obtained by careful selection. They are usually white- or yellow-fleshed, conical in shape, and grow with the root entirely underground. The sugar content now ranges from 10 or 11 to 16, 18, or even 20 p.c.

Roots not exceeding 1½ to 2 lbs. in weight are preferred. A deep medium loam containing a fair proportion of lime is the soil best suited for their growth. Nitrogenous manuring must be only sparingly done, or the roots become watery and deficient in sugar.

It is difficult to give the typical composition of sugar beets, since their sugar content varies so greatly with variety of plant, season, size of root, cultivation, and manuring. Small roots are almost invariably richer than large ones, other things being equal; a dry period during the ripening and maturing of the roots is also favourable to sugar formation; well-tilled soil, regularity of shape of root, and suitable manuring, are all important factors in determining the yield of sugar.

There is evidence that the careful selection of beets for sugar production has altered the plant considerably, so far as content of ash is concerned (Schneidewind, Bied. Zentr. 1900, 29, 81). The proportion of ash is much lower than formerly, the quantity of potash is only about half of what it was, while the soda has doubled; magnesia has remained unchanged, while phosphoric acid is less.

According to Kellner, the average composition of sugar beets is: Water, 75 p.c.; crude protein, 1·3 p.c.; fat, 0·1 p.c.; soluble carbohydrates, 21·4 p.c.; fibre, 1·5 p.c.; ash, 0·7 p.c. In addition to the sugar content, the purity coefficient (the ratio of cane sugar to total sugar) is of importance (*see* SUGAR).

The leaves of mangolds and sugar beets contain much oxalic acid, up to 8 p.c. of the dry matter (Stoklasa, Bied. Zentr. 1901, 30, 393), and their ash is rich in lime, magnesia, and soda. They contain about 84 p.c. water, 2·3 p.c. nitrogenous matter, 0·4 p.c. ether extract, 7·4 p.c. soluble carbohydrates, 1·6 p.c. fibre, and 4·8 p.c. ash.

They are sometimes used as cattle food, either in the fresh or dried condition, or sometimes as silage. In order to prevent ill effects from the oxalic acid present, it is recommended to sprinkle powdered calcium carbonate on the leaves before giving them to animals. About 1 lb. calcium carbonate to 1000 lbs. of leaves is sufficient (Kellner). The leaves are sometimes dried by artificial heat, and then furnish a valuable food, equal to meadow hay. H. I.

BEET-ROOT GUM *v.* GUMS.

BEHENIC ACID $C_{21}H_{43}COOH$ is contained as a glyceride in oil of ben, obtained from the seeds of *Moringa oleïfera* (Völcker, Annalen, 64, 342), and has been prepared by reduction of iodobehenic acid, obtained from erucic acid (Fileti and Ponzio, Gazz. chim. ital. 23, ii. 392; 27, ii. 798); m.p. 84°.

BELLADONNA. (Fr. *Belledame.*) The *Atropa belladonna* (Linn.), or deadly nightshade. A poisonous plant of the *Solanaceæ* order. Employed in medicine as an anodyne, &c., and for dilating the pupil. The name appears to have been derived from the circumstance of its employment in an Italian cosmetic. Its physiological action is due to *atropine* (*v.* VEGETO-ALKALOIDS).

BELLITE. An explosive prepared by mixing a nitrate with a nitro- compound such as dinitrobenzene, trinitronaphthalene, or nitrotoluene, and then subjecting the mixture to a temperature of from 50° to 100° (Eng. Pat. 13690, Nov. 10, 1885; *v.* EXPLOSIVES).

BELLITE. This name has also been used (W. F. Petterd, 1905) for an incompletely determined mineral, described as a chromo-arsenate of lead, and occurring as bright-red or yellow velvety tufts, or as powdery encrustations, at Magnet in Tasmania. L. J. S.

BELL-METAL. An alloy of copper and tin used in the manufacture of bells. Contains from 3 to 4 parts of copper to 1 part of tin.

BELL-METAL ORE *v.* STANNITE.

BENGALINE *v.* AZO- COLOURING MATTERS.

BENGAL LIGHTS. These fires may be made by mixing potassium chlorate, carbon, antimony sulphide, strontium nitrate, &c., together in suitable proportions; but all such mixtures of potassium chlorate and sulphur are dangerous from their tendency to inflame spontaneously owing to sulphur frequently containing sulphuric acid. Saunders suggests that 120 grains of potassium bicarbonate should be added to each pound of sulphur to neutralise the free acid.

An improvement in the manufacture of Bengal lights has been suggested by Chertier (Wagner's Jahr. 24, 464), who obtains a smokeless and odourless fire by melting shellac and adding, with continuous stirring, the nitrate. The proportions given are: for red fires, one part of shellac to five of strontium nitrate; for green, one of shellac to five of barium nitrate; and for yellow, one of shellac to three of sodium nitrate. They burn slowly, and are well adapted for theatres, &c.

C. Schmidt has patented (D. R. P. 34020, 1885) the following process. From 1 to 10 grams of magnesium dust are added to 100 grams of collodion, and 3 grams of barium or strontium chloride are added. On evaporation of the ether, thin plates are obtained which burn with great brilliancy.

Another formula recommended by a German firm is, for white fires, to fuse one part shellac with six barium nitrate, grind and mix with 2·5 parts magnesium powder. For red fires, five parts strontium nitrate is used instead of the barium nitrate. These mixtures can be made into ribbons or charged into thin zinc tubes so as to make torches (Dingl. poly. J. 256, 518). (*See* also FLASH LIGHTS; PYROTECHNY.)

BENITOITE. This interesting mineral is an acid titano-silicate of barium $BaTiSi_3O_9$, and forms beautiful sapphire-blue, transparent crystals suitable for cutting as gems. The crystals afford the only known example (except Ag_2HPO_4 (H. Dufet, 1886)) of the ditrigonal-bipyramidal class. Sp.gr. 3·64–3·67; H. 6½. The dichroism is intense, the ordinary ray being colourless, and the extraordinary ray greenish-blue to indigo-blue. The mineral was first found (and described by G. D. Louderback) in 1907. near the source of the San Benito river in San Benito co., California, the crystals occurring embedded in natrolite veins traversing schistose rocks. L. J. S.

BENJAMIN, GUM, *v.* BALSAMS.

BEN OIL, Behen Oil, is obtained from the seeds of the *Ben nut*, from *Moringa pterygosperma* (*oleïfera*) and *Moringa aptera* (Gärt.). The Moringa trees are indigenous to India, Arabia, and Syria, and were introduced to Jamaica from the East Indies in 1784. *Moringa pterygosperma* has also been found in Northern Nigeria and Dahomey. Ben oil has a slightly yellowish colour, is odourless, and has a sweetish taste. The oil consists of the glycerides of oleic, palmitic, and stearic acids; it also contains a solid acid of high melting-point, which, according to Völcker (Annalen, 64, 342), is identical with behenic acid, of the melting point 76°; possibly the solid acid is identical with arachidic acid. In the East, ben oil is used for cosmetic purposes it is also employed in the 'maceration' process for extracting perfumes from flowers. In the West Indies the oil is used for edible purposes. The statement contained in the older literature, that ben oil does not turn rancid, and that it is for that reason the best lubricating oil, is erroneous (see Chemical Technology and Analysis of Oils, &c., ii. 307). J. L.

BENZACETIN *v.* SYNTHETIC DRUGS.

BENZAL CHLORIDE. *Benzylidene chloride, Benzidene chloride* (*v.* TOLUENE, CHLORINE DERIVATIVES OF).

BENZALDEHYDE C_7H_6O or $C_6H_5{\cdot}CHO$. *Benzoic aldehyde, Benzoyl hydride. Ethereal,* or *volatile,* or *essential oil of bitter almonds. Essence of bitter almonds.* (*Aldehyde benzoïque,* Fr.; *Bittermandelöl,* Ger.) Mortrès showed, in 1803, that, in addition to the fatty oil, a volatile oil could be obtained from bitter almonds; but pure benzaldehyde was first isolated, its composition determined, and its reactions studied, by Liebig and Wöhler in 1837 (Annalen, 22, 1). Benzaldehyde is not contained, as such, in bitter almonds: it is produced by the action of a soluble ferment, *emulsin* (also termed *synaptase*), present in the almond, on *amygdalin* $C_{20}H_{27}NO_{11}$. In this fermentation, which occurs when the bruised almonds are mixed with cold water, the amygdalin is hydrolysed, yielding benzaldehyde, together with hydrocyanic acid and glucose:

$$C_{20}H_{27}NO_{11}+2H_2O=C_7H_6O+HCN+2C_6H_{12}O_6$$

If boiling water is used, the ferment is destroyed and the reaction does not take place. Peach kernels and kernels of other stone fruits containing amygdalin also yield benzaldehyde. It occurs, ready formed, in the leaves of the cherry laurel (*Prunus laurocerasus*), of the bird cherry (*Prunus padus*), and of the peach (*Amygdalus persica*).

Preparation.—1. *From bitter almonds.* The bitter almonds (or more rarely, peach kernels) are ground and then cold-pressed, to extract the fatty oil. The press cake is made into a thin cream with cold water, introduced into a still, allowed to stand for 24 hours, and then distilled either by blowing in superheated steam, or, less advantageously, over a fire, in which case mechanical stirring must be employed to prevent the charring of the vegetable matter. The distillation is continued as long as the distillate appears milky. Most of the crude benzaldehyde separates as an oily layer under the aqueous distillate; some, however, remains in solution and may be recovered by distilling the aqueous liquid, when the benzaldehyde passes over with the earlier portions.

Michael Pettenkofer (Annalen, 122, 77) modifies the foregoing process as follows:—12 parts of the coarsely powdered press cake are added to 100–120 parts of boiling water, stirring during the process, and the mixture is kept boiling for about half an hour. In this way all the amygdalin is obtained in solution. The liquid is then allowed to cool; 1 part of ground bitter almonds, suspended in 6–7 parts of cold water, is added, and after standing for 12 hours the whole is slowly distilled. According to Pettenkofer, the maximum yield of benzaldehyde is thus obtained, no amygdalin remaining undecomposed. Pelz, however, states (J. 1864, 654) that the yield of benzaldehyde in this process is no greater than is obtained by macerating merely the above-mentioned 1 part of ground bitter almonds with cold water and then distilling.

The oil prepared by either of these methods contains hydrocyanic acid, from which it may be freed by fractional distillation, the hydrocyanic acid coming over with the first part of the distillate. The hydrocyanic acid may also be removed without distillation by shaking the oil with a mixture of milk of lime and ferrous sulphate (Liebig and Wöhler). The purest benzaldehyde is obtained by shaking the crude

product with 3–4 times its volume of a concentrated solution of sodium bisulphite, washing the crystals of the double compound

$$(C_7H_6O,NaHSO_3)_2H_2O$$

with alcohol, recrystallising them from water, and distilling them with a solution of sodium carbonate (Bertagnini, Annalen, 85, 183; Müller and Limpricht, *ibid.* 111, 136).

2. *From toluene.* At the present day benzaldehyde is generally prepared artificially from chlorinated derivatives of toluene. The following are the chief processes that have been proposed:—

Lauth and Grimaux (Bull. Soc. chim. [2] 7, 105) boil 1 part of benzyl chloride $C_6H_5\cdot CH_2Cl$, 1½ parts of lead nitrate (or copper nitrate), and 10 parts of water with a reflux condenser for several hours, passing a current of carbon dioxide through the apparatus to prevent oxidation. Half the liquid is then distilled off, and the oil, which separates in the distillate, is rectified. The product, which consists mainly of benzaldehyde, may be further purified by converting it into the bisulphite compound.

H. Schmidt (D. R. P. 20909; J. Soc. Chem. Ind. 1883, 274) chlorinates boiling toluene until it attains a sp.gr. of 1·175, when it consists essentially of a mixture of 2 mols. of benzyl chloride with 1 mol. of benzal chloride. This product is boiled with six times its volume of water and a quantity of powdered black oxide of manganese containing two atoms of available oxygen to the above molecular proportion. The reaction is supposed to take place according to the equation

$$2C_6H_5\cdot CH_2Cl+C_6H_5\cdot CHCl_2+2MnO_2 = 3C_6H_5\cdot CHO+2MnCl_2+H_2O.$$

The product is steam-distilled, and the aldehyde purified in the usual way. A mixture of benzyl bromide and benzal bromide may be substituted for the chlorine compounds.

Another method now generally employed consists in heating benzal chloride with milk of lime under pressure.

$$C_6H_5\cdot CHCl_2 + Ca(OH)_2 = C_6H_5\cdot CHO + CaCl_2 + H_2O.$$

According to Espenschied (D. R. P. 47187), the reaction takes place under ordinary pressures if insoluble substances such as chalk or barium sulphate are added along with the milk of lime, so as to produce an emulsion of the benzal chloride.

E. Jacobsen (D. R. P. 11494 and 13127; Ber. 13, 2013, and 14, 1425) heats benzal chloride with an organic acid (or an ethereal salt of an organic acid) and a metallic chloride, oxide, or sulphide. Thus benzal chloride, when heated on the water-bath with acetic acid and a little zinc chloride, yields benzaldehyde, acetyl chloride, and hydrochloric acid

$$C_6H_5\cdot CHCl_2+CH_3\cdot CO_2H = C_6H_5\cdot CHO+CH_3\cdot COCl+HCl.$$

The acetyl chloride, owing to its much lower boiling-point, may be readily removed from the benzaldehyde by distillation.

Benzaldehyde can be prepared by oxidising benzyl aniline to benzylidene aniline, which, on addition of acids, splits into benzaldehyde and aniline. For this purpose 100 kilos. of benzyl aniline, and from 500–1000 litres of water are placed in a large retort fitted with an agitator; during agitation and boiling the following mixture is gradually run in during a few hours: potassium or sodium bichromate, 50 kilos.; water, 200 litres, acidulated with hydrochloric acid (20°B.), 165 kilos., or its equivalent of sulphuric acid; distillation ensues, water and benzaldehyde coming over. The nitrobenzaldehydes may be obtained by substituting the corresponding nitrobenzylaniline. Another method consists in oxidising the salt of the benzylaniline sulphonic acid to the benzylidene compound, and then treating it with the salt of an aromatic base, followed by hydrochloric acid. The aldehyde is formed, and the aromatic base can be recovered and used for another operation (Farb. vorm. Meister, Lucius and Brüning, Eng. Pat. 10689 and 30118; D. R. P. 110173; J. Soc. Chem. Ind. 1897, 558, and 1899, 36). It has been prepared by passing a current of air charged with the vapour of toluene through a chamber containing a catalyser such as oxide of iron, and heated between 150° and 300°. By substituting porous carbon for oxide of iron and using a higher temperature, benzoic acid may be obtained (Chavy, Delage, and Woog, Fr. Pat. 379715; J. Soc. Chem. Ind. 1907, 1254; Ipatieff, Ber. 1908, 993).

It has also been prepared by the oxidation of benzyl aniline, or benzyl toluidine with chromic acid mixture or with potassium permanganate solution in acetone (D. R. PP. 91503, 92084; Frdl. iv. 129, 131).

It has also been prepared from phenyl magnesium bromide and orthoformic ester (Farb. vorm. Fried. Bayer & Co. D. R. P. 157573; Chem. Zentr. 1905, i. 309). By using 15 grams of magnesium, 100 grams of bromobenzene, and 60 grams of orthoformic ester, a 90 p.c. yield can be obtained (Bodroux, Compt. rend. 1904, i. 92). It has been prepared by the oxidation of toluene with manganese dioxide and sulphuric acid (Soc. Chim. des Usines du Rhône, D. R. PP. 101221 and 107722; Chem. Zentr. 1899, i. 959; 1900, i. 1113), or by heating toluene with nickel oxide (Bad. Anilin u. Sod. Fab. D. R. P. 127338; Chem. Zentr. 1902, i. 150).

It has been prepared by heating benzal chloride with water at 90°–95° in the presence of small quantities of iron or salts of iron (Schultze, D. R. PP. 82927, 85493; Frdl. iv. 143, 145); by passing a stream of carbon monoxide and hydrochloric acid gas (2:1) through a cooled mixture consisting of equal weights of aluminium bromide and benzene, and $\frac{1}{10}$ their weight of copper chloride, a solid mass is obtained: this is decomposed by ice water, extracted with ether, and fractionated. The yield is 85–90 p.c. (Reformatsky, D. R. P. 126421; Chem. Zentr. 1901, i. 1226; ii. 1372).

Benzaldehyde has also been prepared by the electrolytic reduction of benzoic acid or its salts. An electrode of finely divided graphite and benzoic acid is employed as the cathode of the cell, the anode being of lead or platinum. The solution in the cell is 20 p.c. sulphuric acid, saturated with benzoic acid, the current used is 1·5 amp. per sq. dcm., and 12–15 volts (Mithack, D. R. P. 123554; Chem. Soc. Abstr. 1902, i. 291). Mettler (Ber. 1908, 4148) uses a sodium-amalgam electrode; and Moest (D. R. P. 138442; Chem. Zentr. 1903, i. 370) electrolyses a solution of sodium phenylacetate.

A method has been described for purifying benzaldehyde by dissolving it in sulphurous acid and precipitating the bisulphite compound by adding potassium chloride (Chem. Fab. Greisheim-Elektron, D. R. P. 154499; Chem. Zentr. 1904, ii. 965).

Other modes of formation.—Benzaldehyde is also formed in the following reactions, which, however, are not of practical importance. By distilling a mixture of calcium benzoate and calcium formate (Piria, Annalen, 100, 105); by the oxidation of benzyl alcohol (Cannizzaro, Ann. Chim. Phys. [3] 40, 234); of cinnamic acid (Dumas and Peligot, Annalen, 14, 50; Harries, Ber. 1903, 1296); or of stilbene (Harries, *l.c.*); by the reduction of benzoic acid, either with sodium amalgam in acid solution (Kolbe, Annalen, 118, 122), or by passing its vapour over heated zinc-dust (Baeyer, Annalen, 140, 296); by treating toluene with chromyl chloride and then with water (Étard, Ann. Chim. Phys. [5] 22, 225); by treating 1 molecule of benzal chloride with slightly more than 2 molecules of acetic acid (Béhal, Compt. rend. 148, 179); by acting on benzophenoneoxime with phosphorus pentasulphide, and decomposing the thiobenzanilide thus formed with boiling alkali and zinc-dust (Cuisa, Chem. Zentr. 1907, i. 28).

Properties.—Benzaldehyde is a colourless, strongly refractive liquid with a pleasant aromatic odour, boiling at 179°–180°, and solidifying at −13·5° (Pictet, Compt. rend. 119, 955; Altschul and Schneider, Zeitsch. physical. Chem. 1895, 24); sp.gr. 1·0504 15°/4° (Mendeléeff, J. 1860, 7). It is soluble in 300 parts of water, and miscible in all proportions with alcohol and ether. It is non-poisonous, the poisonous properties of ordinary oil of bitter almonds being due to the presence of hydrocyanic acid. Its magnetic rotatory power has been studied by Perkin (J. Chem. Soc. 1896, 1064).

Reactions.—Benzaldehyde readily undergoes oxidation; thus it absorbs oxygen from the air, forming benzoic acid. The presence of hydrocyanic acid protects it from oxidation; according to Dusart (Bull. Soc. chim. 8, 459), it is therefore usual to add hydrocyanic acid to artificial benzaldehyde. Taken internally, benzaldehyde is oxidised in the organism, reappearing in the urine as hippuric acid and benzamide. Aqueous *caustic potash* converts it into benzoic acid and benzyl alcohol

$$2C_6H_5\cdot CHO + KOH = C_6H_5\cdot CO_2K + C_6H_5\cdot CH_2OH$$

It forms crystalline compounds with the *bisulphites of the alkali metals*; thus;

$$(C_7H_6O,NaHSO_3)_2H_2O.$$

Under the influence of dehydrating agents, it readily undergoes condensation with various other substances; thus when heated with *acetic anhydride and dry sodium acetate* it yields cinnamic acid

$$C_6H_5\cdot CHO + CH_3\cdot CO_2H = C_2H_5\cdot CH:CH\cdot CO_2H + H_2O$$

(Perkin, J. Chem. Soc. 31, 389); cinnamic acid is also obtained from *ethyl acetate* and benzaldehyde (Claisen, Ber. 1890, 976; Farb. vorm. Meister, Lucius and Brüning, D. R. P. 53671; Ber. 1891, Ref. 180). With *dimethylaniline* in presence of zinc chloride it forms the compound $C_6H_5\cdot CH(C_6H_4\cdot NMe_2)_2$, the leuco-base of benzaldehyde green which, by oxidation is converted into that colouring matter (O. Fischer, Ber. 11, 950).

With pyrogallol benzaldehyde forms dyestuffs of the triphenylmethane series (Hofmann, Ber. 1893, 1139), and with chloracetopyrogallol a golden-yellow dyestuff (Kusselkaul and Kostanecki, Ber. 1896, 1886). By heating benzaldehyde with a little sulphur in a sealed tube, stilbene and benzoic acid are formed (Barbaglia and Marquardt, Ber. 1891, 1881).

Derivatives.—The most important derivatives are the sulphonic acids, which are the parent substances of various dyestuffs (Gnehm and Schüle, Annalen, 299, 347). Benzaldehyde *o*-sulphonic acid (Kafa, Ber. 1891, 791; Wallach and Wüster, Ber. 1893, 150; Gnehm and Schüle, Annalen, 1898, 24; D. R. P. 88952), Benzaldehyde *p*-sulphonic acid (Farb. vorm. Sandoz, D. R. P. 154528; Chem. Zentr. 1904, ii. 1269).

Impurities and adulterations.—Benzaldehyde very frequently contains hydrocyanic acid, either originally present or subsequently added (*v. supra*), and benzoic acid, formed by spontaneous oxidation. The artificial product generally contains chlorinated benzaldehydes. Alcohol, ethereal oils, and nitrobenzene are sometimes fraudulently added; the latter substance resembles benzaldehyde in smell.

In order to test the purity of a sample of benzaldehyde, the sp.gr. and boiling-point should first be determined, as both of these are altered by the presence of impurities. The substance should also dissolve without residue in a solution of sodium bisulphite.

Of the impurities above mentioned, hydrocyanic acid may be detected by distilling the oil and then testing the first portions of the distillate by the Prussian-blue test; chlorine compounds, by heating the oil with metallic sodium, when sodium chloride will be formed, in which the chlorine can be detected by silver nitrate, taking care, however, to distinguish between silver chloride and silver cyanide, as this latter will be formed if hydrocyanic acid or nitrobenzene is present; alcohol, by the iodoform test; and ethereal oils or nitrobenzene, by dissolving the sample in sodium bisulphite, when these admixtures remain behind. Bourgoin (Ber. 5, 293) tests for nitrobenzene in benzaldehyde by mixing the sample with twice its volume of caustic potash: if nitrobenzene is present, the mixture turns green, and on adding water the liquid forms two layers, of which the under layer is yellow and the upper green, this latter turning red on standing for some hours.

Estimation.—The reagent employed consists of 1 c.c. of freshly redistilled phenylhydrazine, 0·5 c.c. glacial acetic acid dissolved in 100 c.c. distilled water. The liquid containing the benzaldehyde is heated on the water-bath for half an hour, set aside for 12 hours, and filtered through a Gooch crucible, dried over conc. sulphuric acid, and weighed. Weight of phenyl hydrazone ×0·5481 gives the amount of benzaldehyde present. Small quantities may be satisfactorily estimated by this method (Hérissey, J. Pharm. 1906, 60; Dennis and Dunbar, J. Soc. Chem. Ind. 1099, 488). Another method consists in estimating benzaldehyde colorimetrically with fuchsin decolourised with sulphurous acid (Woodman and Lyford, J. Amer. Chem. Soc. 1908, 1607).

SUBSTITUTION DERIVATIVES OF BENZALDEHYDE.

o-Nitrobenzaldehyde. It may be prepared by the oxidation of the dimercury derivative of *o*-toluene (Reissert, D. R. P. 186881; Chem. Soc. Abstr. 1907, i. 1046; Kalle & Co., D. R. P. 199147; Chem. Soc. Abstr. 1909, i. 76); by the oxidation of *o*-nitrotoluene with manganese dioxide or by passing the vapour of the hydrocarbon over manganese dioxide heated to 210°–250° (Gilliard, Monnet and Cartier, D. R. P. 101221; Chem. Zentr. 1899, i. 960; Bad. Anil. u. Sod. Fab., Eng. Pat. 21947; J. Soc. Chem. Ind. 1900, 892); by the oxidation of *o*-nitrotoluene with nickel oxide, nickel chloride, and hypochlorite (Bad. Anil. u. Sod. Fab., D. R. P. 127388; Chem. Zentr. 1902, i. 150); by the oxidation of *o*-nitrobenzylaniline (*q.v.* benzaldehyde); by the oxidation of *o*-nitrobenzylalcohol and its esters (Eug. Fischer, D. R. P. 48722; Frdl. ii. 98; Kalle & Co., D. R. PP. 104360, 106712; Chem. Zentr. 1899, ii. 950; 1900, i. 885); by the hydrolysis of *o*-nitrobenzaldehyde diacetate, which is obtained by the oxidation of *o*-nitrotoluene with a mixture of acetic anhydride, acetic acid, and sulphuric acid (Thiele and Winter, Annalen, 311, 356; Fried. Bayer & Co., D. R. P. 121788; Chem. Zentr. 1901, ii. 70).

Properties.—Large yellow needles, m.p. 43·5°–44·5°. When treated with acetone and caustic soda it yields indigotin (Baeyer, Ber. 15, 2856). With methyl- and ethyl-aniline or their sulphonic acids it condenses to form leucobases of blue-green triphenyl methane dyestuffs (Clayton Aniline Co., D. R. P. 108317; Chem. Zentr. 1900, i. 1081).

m-Nitrobenzaldehyde. It may be prepared by dissolving 1 volume of benzaldehyde in a mixture of 5 volumes of fuming nitric acid, and 10 volumes of sulphuric acid, precipitating by addition of water and recrystallising from dilute alcohol (Widmann, Ber. 13, 678; Bertagnini, Annalen, 79, 260).

Properties.—Pale-yellow needles, m.p. 58°. It condenses with the sulphonic acids of the tertiary aniline bases to yield dyestuffs (Kalle & Co., D. R. P. 73147, Frdl; iii. 85).

p-Nitrobenzaldehyde. It is prepared by similar methods to those by which the ortho-compound is obtained (D. R. PP. 91503, 92084, 93539; Frdl. iv. 129); by heating *p*-nitrobenzylalcohol with copper oxide or other metallic oxides (Schmidt, D. R. P. 15881; Frdl. i. 60).

Properties.—Colourless prisms, m.p. 106°. It condenses with benzene and its homologues by addition of sulphuric acid to form *p*-nitrotriphenylmethane (Stolz, D. R. P. 40340; Frdl. i. 58); with secondary and tertiary amines to form alkyl- and aryl- derivatives of *p*-nitrodiaminotriphenylmethane (O. Fischer, D. R. PP. 16766, 16707; Frdl. i. 54); and with the sulphonic acids of tertiary aniline bases (Kalle & Co., D. R. P. 73147; Frdl. iii. 86). The sulphonic acid of *p*-nitrobenzaldehyde is prepared by the oxidation of *p*-nitrotoluene *o*-sulphonic acid, and from it blue and bluish-red dyestuffs of the triphenylmethane series are easily obtainable (Green and Wahl, Eng. Pat. 21825; J. Soc. Chem. Ind. 1898, 915).

o-Chlorbenzaldehyde. It is prepared by the oxidation of *o*-chlortoluene with manganese dioxide and sulphuric acid (Gillard, Monnet et Cartier, D. R. P. 101221; Chem. Zentr. 1899, i. 960), by extraction from the products of the incomplete chlorination of *o*-nitrotoluene (Kalle & Co., D. R. PP. 110010, 115516; Chem. Zentr. 1900, ii. 460, 1168).

Properties.—It is a liquid boiling at 213°–214°; sp.gr. 1·29 at 8°. By heating with sulphite it is converted into benzaldehyde *o*-sulphonic acid (Geigy & Co., D. R. P. 88952; Frdl. iv. 113). It is easily condensed with aromatic secondary and tertiary amines to yield dyestuffs of the triphenylmethane group (Geigy & Co., D. R. P. 94126; Chem. Zentr. 1898, i. 296). By sulphonation, 1 : 3 : 6-chlorbenzaldehyde sulphonic acid is produced, which when condensed with secondary or tertiary amines and then oxidised yields greenish-blue or blue dyestuffs (Soc. Chem. Ind. of Basle, Eng. Pat. 25128; J. Soc. Chem. Ind. 1897, 137; Gnehm and Schüle, Annalen, 299, 347).

m-Chlorbenzaldehyde. It is obtained from *m*-nitrobenzaldehyde by replacing the nitro-group by chlorine (Erdmann and Schwechten, Annalen, 260, 259; Eichengrün and Einhorn, *ibid.* 262, 135). It crystallises in prisms, m.p. 17°, and boils at 213°.

p-Chlorbenzaldehyde. It is associated with the ortho- compound in most preparations, and may be obtained from the mixture by sulphonating the ortho- compound by treatment with fuming sulphuric acid (Gesel. f. Chem. Ind., D. R. P. 98229; Chem. Zentr. 1898, ii. 743); by nitrating the ortho- compound with nitric and sulphuric acids, and steam-distilling the para-compound (Gesel. f. Chem. Ind., D. R. P. 102745; Chem. Zentr. 1899, ii. 408); by fractional distillation (Farb. vorm. Meister, Lucius and Brüning, D. R. P. 207157; J. Chem. Soc. Abst. 1909, i. 307). It is a crystalline solid, melting at 47·5° and boiling at 213°–214°.

Of the **dichlorbenzaldehydes** the 2 : 5- and 2 : 6-dichlor- compounds are the parent substances of many dyestuffs. **2 : 5-dichlorbenzaldehyde** (Gnehm and Bänziger, Ber. 1896, 875; Schüle, Annalen, 299, 34). **2 : 6-dichlorbenzaldehyde** (Anil. Fabw. und Ext. Fabrik., D. R. P. 199943; Chem. Soc. Abstr. 1908, i. 986).

Hydroxybenzaldehydes (*q.v.*) **Salicylaldehyde.**

BENZALDEHYDE GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BENZAMIC ACID *v.* AMINO-ACIDS (aromatic).

BENZAURIN *v.* AURIN.

BENZENE AND ITS HOMOLOGUES.

Benzene. (*Benzol, Benzole,* Fr.; *Benzol,* Ger.) The name of this substance was derived in its original form from that of gum benzoïn, probably as *benzoïn oleum,* hence *benzole,* which latter form is still in use amongst nearly all distillers and users of it both in this country and on the Continent. In more strictly scientific literature, however, the name *benzene* has now become generally accepted, and the systematic termination *-ene* is employed in the names of its various homologues, as toluene, xylene, cymene, etc.

Pure benzene is a *limpid, colourless, highly* refracting liquid at ordinary temperatures. Its sp.gr. at 0° is 0·8991 (Kopp), 0·90023 (Adrieenz), and at 15° 0·8841 (Mendeléeff).

Its refraction index for the D line at 15·2° is 1·4957 (Adrieenz); at 9°, 1·4593 for A, 1·5050 for

D, 1·5037 for H (Gladstone); at 8·5°, 1·50381 for H_a (Perkin, Chem. Soc. Trans. 1900, 77, 273).

When surrounded by ice it becomes solid, and if crystallisation is allowed to take place slowly, rhombic crystals are produced, the axes of which, *a*, *b*, *c*, are 0·891, 1, 0·799 (Groth). The solid melts at 5·4°.

It contracts on solidification, the difference in the specific volume of the liquid and solid $v_l - v_s = \Delta v$ is between 0·1219 and 0·1304 at 5·35° (Heydweiller, Ann. Phys. Chem. 1897, (iii.) 61, 527).

It exhibits no absorption lines or bands in the visible portion of the spectrum. Beyond H, however, photographs show a series of four bands covering the region lying between W. L. 3171 and 2190 tenth-metres. The methylated benzenes, toluene, and the three xylenes exhibit a similar absorption, requiring, indeed, very careful measurement to distinguish one from the other (Hartley, Chem. Soc. Trans. 1885, 47, 685; Proc. Roy. Soc. 1908, 80, A, 162; Hartley and Dobbie, Chem. Soc. Trans. 1898, 73, 695; Baly and Collie, *ibid.* 1905, 87, 1332; Friederichs, Zeitsch. photochem. 1905, 3, 154; Grebe, *ibid.* 376; Mies, *ibid.* 1909, 7, 357; 1910, 8, 287).

Benzene is an excellent solvent, easily dissolving caoutchouc and asphaltum, if they have not been exposed to light, though the protective effect of the light on the asphaltum is but slight, and prolonged treatment with benzene causes it to dissolve. Nearly all the gum resins, sulphur, phosphorus, fats, oils, most of the natural alkaloids, and many other organic compounds, are soluble in it. It has also, in common with carbon disulphide, the property of dissolving iodine with production of a violet solution.

Benzene is itself soluble to a very slight extent in water, considerably more so in alcohol, whilst ether, glacial acetic acid, and carbon disulphide, dissolve it readily.

Benzene boils under normal pressure at 80·36° (Regnault). For benzene from coal tar, Adrieenz found 80·53° to 80·62°; and for that obtained from benzoic acid prepared from gum benzoïn, 80·60° to 80·67°. Its specific heat at temperatures between −185° and +20° is 0·176 (Nordmeyer and Bernouilli, Ber. Deut. physikal. Ges. 1907, 5, 175) and at 94° is 0·4814 (Schlamp, Ann. Phys. Chem. .1896, (iii.) 58, 759). The latent heat of vaporisation is 94·37 (Griffiths and Marshall, Phil. Mag. 1896, (v.) 41, 1) or 94·93 (Campbell Brown, Chem. Soc. Trans. 1905, 87, 265).

The vapour when inhaled produces giddiness and ultimately insensibility.

Benzene forms with picric acid the molecular compound $C_6H_2(NO_2)_3OH,C_6H_6$, which melts with decomposition at 90°.

Oxidising agents, such as potassium permanganate or manganese dioxide and sulphuric acid, convert it into formic, propionic, and oxalic acids, together with small quantities of benzoic and phthalic acids, the latter substances being produced by the simultaneous oxidation of formic acid and benzene, the process of condensation resembling that occurring in the conversion of dimethylaniline into methyl violet. When strongly heated in sealed tubes or when passed slowly through strongly heated open tubes, condensation and decomposition go on together, acetylene, diphenyl, diphenylbenzene, etc., being formed with evolution of hydrogen and deposition of carbon.

There can be little doubt that toluene and xylenes can also be produced in this way, and since Berthelot has shown that toluene and xylene when passed through strongly heated tubes can produce anthracene and naphthalene, and since he also obtained anthracene by so treating a mixture of benzene and ethylene, we may assume that if benzene is *not* the mother substance of the whole series of hydrocarbons obtained from coal tar, it is yet capable, under proper conditions, of generating all the others.

When chlorine acts on pure benzene in sunshine, benzene hexachloride $C_6H_6Cl_6$ is formed. The substitution of chlorine for hydrogen in the nucleus or benzene ring is a very slow operation if chlorine alone is used, but if in every litre of benzene about 10 grams of iodine are dissolved, and the liquid kept boiling while a brisk current of chlorine is passed into it, substitution readily takes place and chlorinated benzenes are produced. The reaction may be continued until the whole of the hydrogen is replaced with production of hexachlorobenzene C_6Cl_6. Corresponding bromine and iodine compounds, and mono- and *p*-di-fluoro- derivatives are known.

When subjected to the action of strong nitric acid or a mixture of nitric and sulphuric acids, substitution of hydrogen by NO_2 takes place with great ease. If the mixture is kept cool only mononitrobenzene is formed, but if heated, the three dinitrobenzenes are produced, the metadinitro- product (m.p. 89°) always greatly predominating. The ortho- and para- compounds can only be produced in quantity by indirect methods. Trinitrobenzenes can only be obtained by the action of a great excess of a mixture of nitric acid and fuming sulphuric acid.

All the nitro- compounds on reduction with appropriate reagents, such as iron, zinc, or tin, in the presence of acid, preferably hydrochloric and water, yield amino- compounds corresponding with the nitro- compound reduced. Such are aniline $C_6H_5{\cdot}NH_2$, the three diaminobenzenes or phenylenediamines $C_6H_4(NH_2)_2$, etc.

The amino- compounds, by the action of nitrous acid or nitrites in the presence of an excess of acid, preferably hydrochloric, are converted into diazo- compounds. If a diazobenzene salt, *e.g.* $C_6H_5{\cdot}N_2Cl$, is dissolved in absolute alcohol, and the solution heated, the nitrogen is evolved as gas whilst benzene is regenerated. If a diazo- salt is dissolved in water and boiled in the presence of an acid, nitrogen is also evolved and the corresponding phenol is produced.

The diazo- compounds react with certain amino- compounds or phenols, giving rise to the almost innumerable series of colouring matters known as azo- dyes (*q.v.*). Solutions cooled with ice should be employed, and all rise of temperature must be carefully avoided. Under proper conditions some diazo- compounds, however, attack the *amino-* group of amino- compounds, forming diazoamino- compounds such as diazoaminobenzene $C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5$.

These can be made to undergo an isomeric change resulting in the formation of what are known as aminoazo- compounds, of which aminoazobenzene $C_6H_5{\cdot}N:N{\cdot}C_6H_4{\cdot}NH_2$ is a typical example. Such substances, when treated with a reducing agent, split up into an amine and a paradiamine, while diazo- compounds yield hydrazines only, and diazoamino- compounds a mixture of a hydrazine and anamine.

If the nitro- compounds are submitted to the action of alkaline reducing agents in alcoholic solution, such as a mixture of zinc-dust and alcoholic soda, the reaction takes a different course altogether. The action of alcoholic soda and heat alone will convert mononitrobenzene into azoxybenzene $C_6H_5{\cdot}N{-}\underset{\diagdown O \diagup}{}N{\cdot}C_6H_5$; this, by nascent hydrogen, is converted into azobenzene $C_6H_5{\cdot}N:N{\cdot}C_6H_5$, which under the action of the same reagent is still further reduced to hydrazobenzene $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. The latter, when boiled with an acid, is converted into a salt of benzidine (paradiaminodiphenyl)

$$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$$

which is strongly basic compound isomeric with hydrazobenzene.

When heated with concentrated sulphuric acid or treated in the cold with solutions of sulphur trioxide in sulphuric acid, sulphonic acids are produced by substitution of HSO_3 for hydrogen. These are either mono-, di-, or polysulphonic acids, according to the treatment adopted. They are all powerful acids, and form well-defined and generally well-crystallised salts with sodium, potassium, and ammonium, and equally definite, though less easily crystallised salts with calcium, barium, copper, iron, etc. These, especially the sodium or potassium salts, if fused with caustic potash or soda, or heated under great pressure (40 atmospheres) with aqueous soda or potash, are decomposed with production of a sulphite of the alkali metal, and conversion of the benzene residue into the corresponding hydroxy- or phenolic compound.

Only the methyl homologues of benzene will be considered here, as these are the chief ones which occur in coal-tar.

The monomethyl derivative is known as *toluene*, and under all treatments behaves as a completely homogeneous substance.

The dimethyl derivative is known as *xylene*, the substance of that name occurring in coal tar, which occurs as three isomeric compounds: *Orthoxylene*, boiling at 341°–142°, which, when gently oxidised with weak nitric acid, gives a toluic acid melting at 102°; *metaxylene*, boiling at 139°, which gives a toluic acid melting at 106°; *paraxylene*, melting at 15°, and boiling at 138°, giving a toluic acid melting at 178°.

Each of these different xylenes is, however, absolutely identical in percentage composition, and this isomerism is considered to be due to the *configuration* of the molecule, or, in other words, to the positions in space occupied relatively to each other, and to the benzene residue, by the two substituting molecules.

This method of regarding the constitution of benzene and its innumerable series of derivatives is usually, for purposes of discussion, investigation, or explanation, represented by drawing a hexagon to represent the molecule of

benzene, the six angles representing the six groups of CH at any of which substitution is supposed to take place. Since only one monosubstitution compound of a given kind (*i.e.* containing a given substituting group) is known, all the six CH- groups in benzene are supposed to be of equal value. The fact that disubstitution compounds exist in three distinct isomeric modifications (compare the above-mentioned xylenes), is explained in this scheme by the following suppositions as to the relative positions occupied by the substituting groups. First, substitution is supposed to take place at two adjacent angles, *e.g.* 1 and 2, 2 and 3, 4 and 5, &c., in which case the word *ortho-* is prefixed to the name of the substance, as orthodimethylbenzene (commonly called orthoxylene), or orthodichloro-, orthodibromo-, or orthodiamino-benzene, etc. Or the substitution is supposed to take place at two angles not adjacent, but with one interposing, as at 1 and 3, 2 and 4, or 1 and 5, etc. In this case the product is indicated by the prefix meta-, as metadimethylbenzene (commonly called metaxylene, &c. Lastly, the substitution is supposed to take place at opposite angles, such as 1 and 4, 2 and 5, 3 and 6, etc. In such a case the substance is known as a para- compound, as paradimethylbenzene, or paraxylene, paradinitrobenzene, etc.

This theory is due to Kekulé, and satisfactorily agrees with most of the phenomena.

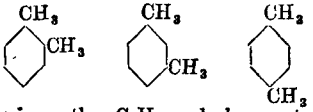
Toluene and xylene generally react under similar conditions in the same way as benzene, producing a similar series of compounds. Since, however, toluene itself is a mono- substituted benzene, mono- substituted toluenes are really di- derivatives of benzene. For instance, there is but one mononitrobenzene, but there are three mononitrotoluenes. There are three dinitro- and three diamino- benzenes, but there are six dinitrotoluenes and six diaminotoluenes, and so on.

It is to be borne in mind that in all substitution derivatives higher than the di- substitution series, the number of possible modifications is greater when the substituting groups are dissimilar than when they are all alike; thus, although there are only three isomeric tri- substitution compounds of the formula $C_6H_3X'_3$ or $C_6H_3Y'_3$, there are six such compounds of the formula $C_6H_3X'_2Y'$.

It follows that the xylenes being di- derivatives, their mono- are tri- derivatives of benzene, and consequently correspond in number with the di- derivatives of toluene.

The introduction of the methyl group, moreover, permits of another kind of substitution which gives rise to a totally different class of compounds from those described above as configurational isomerides, in which substitution takes place not in the benzene nucleus, but in the methyl group itself. Such substitution is said to be *extra-nuclear*.

Thus, as mentioned above, there are three substances having the formula C_8H_{10} known as ortho-, meta-, or para-xylene. These isomerides are represented as dimethylbenzenes of the following configurations:—



but there is another C_8H_{10} only known to occur in one form, and always behaving as a mono-derivative of benzene; this is ethylbenzene

Just as in this case a methyl group has been introduced into the methyl instead of into the nucleus, so chlorine, bromine, etc., may be introduced, and in this manner such compounds as benzyl chloride $C_6H_5 \cdot CH_2Cl$, the di- or trichloride, benzaldehyde, and many others are formed.

The physical properties of toluene greatly resemble those of benzene. As solvents, there is little or no difference in their powers, and though the boiling-point of toluene is so much higher than that of benzene, yet in a current of air at ordinary temperatures it evaporates nearly as quickly.

Toluene is a colourless limpid liquid which solidifies at −94·2° (Ladenburg and Krügel, Ber. 1899, 32, 1818) or −97° to −99° (Archibald and McIntosh, J. Amer. Chem. Soc. 1904, 26, 305). Its specific gravity is less than that of benzene, being at 0° 0·882, at 15° 0·872, its index of refraction at 25·5° is for A 1·4709, D 1·4794, H 1·5090 (Gladstone and Dale), at 8·5° for Hα 1·49891 (Perkin).

Toluene boils constantly at 111°; the vapour has much the same physiological effects as that of benzene, but its odour is decidedly less pleasant. If ingested into the stomach, it is eliminated in the urine as hippuric acid.

Of the three xylenes the meta- is chiefly used in commerce. Orthoxylene boils at 141°–142°. Metaxylene boils at 139°, and its specific gravity is 0·8668 at 19°. Paraxylene boils at 138°, and at 19° its gravity is 0·8621. The two former are liquid at all temperatures down to at least −20°, but paraxylene becomes solid when exposed to a freezing mixture, and when once frozen it only melts at 15°.

The xylenes are distinctly less volatile than toluene and benzene in an air current. The smell of the vapours is unpleasant and pungent, and they possess the power of producing unconsciousness when inhaled.

Both benzene and toluene when prepared from coal tar are accompanied by sulphur compounds known as thiophens. That derived from benzene, no doubt by the action of sulphur from the pyrites of coal at a high temperature during distillation in the gas retort, is represented by the formula C_4H_4S or .

It was isolated in 1882 by V. Meyer, who obtained by constant and repeated agitation with sulphuric acid about 2 kilos. from 2000 kilos. of commercial benzene. It is a colourless liquid, boiling constantly at 84°; sp.gr. at 15° 1·100. In many of its reactions it behaves exactly like benzene.

Two thiotolens corresponding with toluene, i.e. being methylthiophen, are known. They both boil at about 113°, sp.gr. 1·0191. The very minute quantity in which these substances occur renders them of no industrial importance, even as impurities.

Benzene was first isolated by Faraday in 1825, in the liquid separating from condensed oil gas.

It is unnecessary here to describe the processes by which Mitscherlich, D'Arcet, Kopp, and many others obtained benzene, as the first practically industrial process was that of Mansfield, founded entirely at first on Faraday's, and dealing with a similar product as the source, namely, coal tar (Mansfield, Quart. Jour. Chem. Soc. 1848, 1, 244). Mansfield took the lower boiling portion of coal tar, which was then used under the name of naphtha for lighting purposes, and distilled it over a flame in a still provided with a jacketed head and a simple form of dephlegmator made by connecting the upper part of the condensing worm with the still body by an inclined tube. The water in the jacket round the long egg-shaped head partially condensed the vapours rising from the boiling fluid until it reached a temperature of 100°, when those vapours condensable at that temperature were alone affected and returned to the still, those requiring a lower temperature passing on to the worm, and being condensed and collected. Much of the spray carried upward by the vapours was stopped in the head, and what passed it and was condensed in the connecting tube between the still head and the worm flowed into the inclined tube, and found its way back to the body of the still. Finally, when nothing more could pass the boiling water in the jacketed head, this inclined tube, on a cock being fully opened, which during the first part of the process was partially closed, could be made use of to distil over the higher boiling portions.

Such an apparatus could, of course, only effect a rough separation of the oil into a 'benzol' mainly distilling below 100° and a 'naphtha,' most of which would not distil below 100°.

If, however, the water of the water jacket round the head were carefully kept at a stated temperature, say 80°–82°, a much purer product could be obtained. For some years the process was only carried out with the object of getting oils for the Read Holliday lamp, and for the use of rubber manufacturers.

The early demands for 'benzol' for use in the aniline colour industry were confined to what were known as 30 p.c., 50 p.c., and 90 p.c. benzols, which terms were understood to mean that 30, 50, or 90 p.c. by measure of the sample boiled below 100°. Of these the 30 p.c. was mainly used for the production of aniline for red, and the 90 p.c. for aniline for blue. Mansfield had, however, subjected his distillates to a careful but most laborious fractionation in glass retorts, finally obtaining perfectly pure benzene by recourse to freezing and pressure, and he pointed out that 'it is evident that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits are applicable to the separation of benzole from the less volatile fluids of the naphtha' (Reports of the Royal College of Chemistry, 1849, 257).

Mansfield, in fact, in the remarkable paper just quoted, laid the foundations of the whole

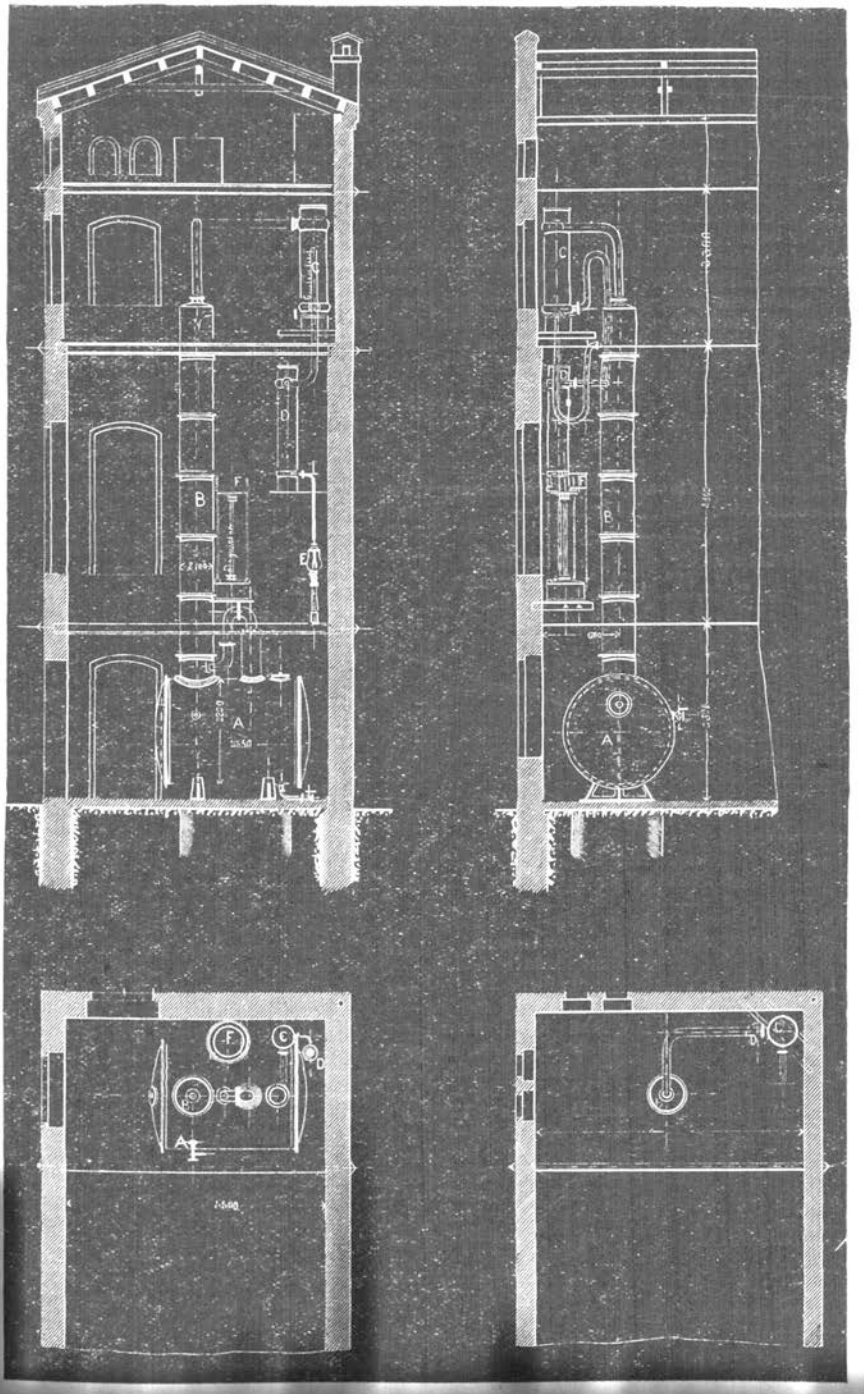


FIG. 1.

A, Still body. B, Analysing column. C, Cooler kept at temperature of distillate wanted. D, Condenser for pure distillate. E, Vase into which distillate flows. F, Automatic regulator.

benzene industry, and his processes with scarcely a change are in use to this day. The departures from them have been one by one abandoned in favour of his method of absolute separation of the light oils into their constituents, and it is not too much to say that had it not been for his terrible death [1] in February, 1855, we should have had the pure hydrocarbons in the market many years ago.

The introduction of the aniline black printing processes and other improvements in the dye industry, however, slowly gave rise to a demand for a purer benzene, while later on a demand for toluene and xylene stimulated the improvement of the distillation process.

The movement was naturally, as Mansfield had suggested, towards the use of such a still as had been introduced by Mr. Coffey in his patent of 1832 and subsequently carried to great efficiency by succeeding generations of spirit distillers. Coupier of Paris appears first to have worked on a large scale in this direction about 1863. He modified the original Mansfield apparatus in the way mentioned above, and showed that at one operation he could separate ordinary 50 p.c. commercial benzol as follows:—

100 *litres yielded*:

44	litres	between	80° and 82°	('Pure benzol')
6	,,	,,	82° ,, 110°	(Crude toluol)
17	,,	,,	110° ,, 112°	('Pure toluol')
5	,,	,,	112° ,, 137°	(Crude xylol)
9	,,	,,	137° ,, 140°	('Pure xylol')
13–14	,,	,,	140° ,, 150°	last runnings.

In addition there were about 6 litres between 62° and 80°, consisting of various impurities such as carbon disulphide, acetonitrile, etc.

Vedlé, Savalle of Paris, and others followed with various improvements in the same direction, Savalle being most generally considered to have produced the best still, though it had two great drawbacks, viz. it was manufactured of copper, which made it very costly, and it was hampered, as far as its condensation arrangements were concerned, by an expensive and useless attempt to use air from a fan driven by steam as a means of cooling the condensers.

The latter attempt was soon given up. In Fig. 1 (p. 443) is seen the apparatus in its latest form as made by the Metallwerke vormals T. Aders, of Magdeburg-Neustadt.

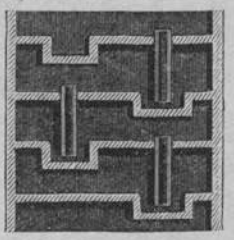


FIG. 2.

The still being charged with the proper quantity of naphtha or crude benzol, which has undergone the necessary washings with sulphuric acid and sodium hydroxide, steam is admitted into the coils, where it circulates, the condensed water escaping through another tube in the usual fashion. As soon as the liquid begins to boil, the vapour ascends into the head *a* and passes through the curved tube *a'* into the bottom of the column B. This contains 25 to 30 flat diaphragms, each pierced with a number of small holes, and one larger, into which is fitted a short wide overflow tube, the end of which stands up about 2 inches above the level of the plate. On the opposite side of the plate is a small depression about 2 inches deep and 4 inches in diameter, into which the overflow tube from the plate above dips, its own tube dipping in the same way into a depression in the plate below. The condensed fluid acts to each overflow tube as a trap (Fig. 2), and prevents the ascent of vapour through it.

The rising vapour condenses rapidly on these plates, and the fluid thus produced, unable to penetrate the small holes through which the hot vapour is rushing, rises to the brim of the overflow tube, and then pours down from plate to plate into the still body. The non-condensed vapour rises through the perforations of the next plate, where it undergoes a similar operation, and so on to the top, the vapour passing away from which has thus been successively washed by bubbling through some thirty layers of fluid, each slightly cooler than the one beneath. Finally, the vapour passes through a surface or multitubular condenser, C, which is provided with a water supply so regulated that its temperature is about that of the boiling-point of the liquid required. The liquid here condensed flows back into the column at a suitable point, while the now purified vapour passes on to the second condenser, D, and is finally completely condensed into the liquid form. Thence it flows into the glass vase E, which is fitted on to a stand-pipe communicating with the distributing-pipes which convey it to the store tanks. The fractions taken should now boil as follows: Benzene, 80°; toluene, 110°; xylene, 140°.

If pure products are required, each fraction is washed with concentrated sulphuric acid, and a washing with soda solution follows. The fraction is introduced into a cast-iron vessel provided with a lid with manhole and inlet pipe. Through the centre passes a vertical shaft rotated by mitre geared wheels. The shaft is provided with arms so arranged that the contents can be thoroughly churned up. A good form of apparatus is seen in Fig. 3. The details need no description except to point out that the screws used to force the fluids through the two vomiting tubes A and A' should be set on the shaft with their helices reversed right and left, so that the lower one causes the lower fluid to rush up, and the upper one the upper fluid to rush down; they thus cause the two currents to meet together violently and thoroughly mingle. The centre shaft may also consist of an Archimedean screw or of a truncated hollow cone. Air agitation is not advisable on account of the loss of benzol which it is apt to cause.

If the fraction is of fairly good quality and has been properly separated from the crude benzol or light oils, the amount of acid required need not be more than one-twentieth of its weight. In some cases, however, where the impurities are difficult to remove, more must be used, and the operation repeated. After the acid has been run off, a washing with enough soda solution to neutralise excess of acid and remove traces of phenols follows, and the fraction is then ready for a second rectification.

If crude naphtha has been used to charge the still, it will have yielded, *inter alia*, 50 p.c. or

[1] Mansfield was burned to death by the boiling over of a benzene still.

90 p.c. benzol according to requirements. On redistillation, 100 parts of the former should yield 45–48 parts of pure benzene, and from 100 parts of the latter 70 parts of pure benzene should be obtained.

When re-rectified, the benzene and toluene

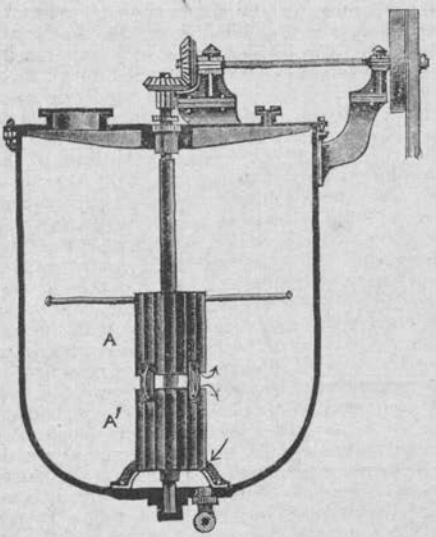


FIG. 3.

should each distil constantly within 0·5° and 1·0° respectively, and the xylene within 2°.

The treatment for obtaining toluene is exactly the same as that described for benzene, the toluene following the benzene from the crude benzol still and being subsequently re-rectified. Toluene is also accompanied by the corresponding thiophen (thiotolen), and requires very careful and thorough washing with sulphuric acid, or it cannot be properly nitrated.

After the separation of the toluene, more or less crude xylene is obtained, and the residue in the still is then cooled and run out. When good crude benzol has been worked, the residue contains a very large quantity of naphthalene, which separates from it when cold, and is known in the works as 'naphthalene salts.' As it has all been brought off from the tar at a low temperature, it is extremely free from higher boiling substances, and very pure naphthalene can be obtained from it with little trouble. Of the rest, some 20–30 p.c. consists of phenol, to which the same remarks apply. The remaining third consists of a mixture of hydrocarbons from which some more xylene could no doubt be recovered, but the bulk of this 'dead oil,' as it is often called, is used for burning. Metaxylene can be prepared from the purified mixed xylenes by agitation with sulphuric acid, as described for benzene and toluene, to remove the thiophens, when a subsequent treatment with its own weight of sulphuric acid converts the metaxylene into a sulphonic acid, which after separation from the insoluble portion is hydrolysed, and metaxylene of great purity obtained.

Valuation of commercial 'pure benzol.'—As stated above, the whole should boil within 0·5° of the correct boiling-point. It should give no crystalline precipitate on standing with a few drops of phenylhydrazine (test for carbon disulphide). When shaken with concentrated sulphuric acid the latter should be only slightly darkened (thiophen or aliphatic hydrocarbons). On shaking with sulphuric acid and a trace of isatin, no blue coloration should be produced (thiophen). On treatment with a mixture of nitric and sulphuric acids, and subsequent distillation in a current of steam, no unnitrated hydrocarbons should be obtained (aliphatic hydrocarbons). Lastly, it should solidify when cooled below 0°.

Pure toluene of commerce should not impart any coloration to sulphuric acid when shaken with it. On shaking 90 c.c. of toluene with 10 c.c. of nitric acid (sp.gr. 1·44) in a stoppered bottle, the acid should assume only a red colour, and remain quite clear and bright, not turning greenish or blackish. (For much information as to the commercial valuation of 'benzols," *see* Lunge, Coal Tar and Ammonia, 4th ed. 1909.)

Nitration of benzene, toluene, etc.—Nitrobenzene first made its appearance in the arts under the name of *essence de myrbane*, manufactured in France by Collas. It was used to scent soap and as a bitter-almond flavouring. Mansfield had taken out a patent for its manufacture in 1847 from coal-tar benzene. The history of its manufacture is interesting, as the difficulties to be encountered were very considerable.

The first really large quantity produced was made by Messrs. Simpson, Maule, & Nicholson, at Kennington, in 1856. They worked at first entirely in glass. Along a bench a row of some twenty bolt-heads, each of about 1 gallon capacity, was ranged, with a convenient water trough at hand. Into each flask from 1 to 2 lbs. of benzene was introduced, and the calculated quantity of the mixed acid, divided up into corresponding portions, stood beside each in a stoneware jug. Commencing with the first flask, a workman next proceeded to add a small quantity of the acid and thoroughly swing round and agitate it with the benzene. As soon as he judged it to be safe to leave this flask, he treated the next in rotation, and so on till the whole series had received its first portion. He now returned to No. 1, and added a second quantity of acid, and this was continued until all were finished. It need scarcely be said that the process was considered a dangerous one, and that any attempt to increase the scale of manufacture was a very serious undertaking. The attempt, however, was made in cast-iron vessels, furnished with mechanical stirrers, and the size of the apparatus was rapidly increased until it attained dimensions at which it was capable of dealing with several hundred pounds weight of benzene.

The usual arrangement now adopted (*see* Fig. 4) is as follows:[1]—

The nitrating pan has a total capacity of 1600 gallons, and is capable of treating 500 gallons or 4420 lbs. of benzol in one charge. It is of cast iron, 1½ inches thick, the sides, from the lid down to a depth of 3 feet, being ¼ inch thicker. The vertical agitating shaft is suspended from the lid on ball bearings, and carries

[1] See Chem. Trade Jour. 1906, 38, 59. The writer is indebted to Messrs. Davis Bros. for permission to reproduce the sketch of the apparatus.

two propellor agitators. The internal cooling pipes consist of two separate coils of thin lead pipe 2 inches diameter, each coil being about 150 feet long. They are supported on circular cast-iron grates or tables, as shown. The coils are spaced out so as to allow free passage of the liquid between them. To direct the upward flow of the liquid, the lower propellor agitator is surrounded by a cast-iron cylinder with large perforations at the bottom to admit the descending liquid. This serves also as a support for the grates and coils. Five hundred gallons of pure benzol are first run by gravity into the machine. The acid-mixing tank, which stands above, is charged with 5000 lbs. of nitric acid, 1·43 sp.gr. or 86°Tw., and 6600 lbs. of sulphuric acid of 96 p.c., and these are thoroughly mixed by air agitation. In some factories the acids are

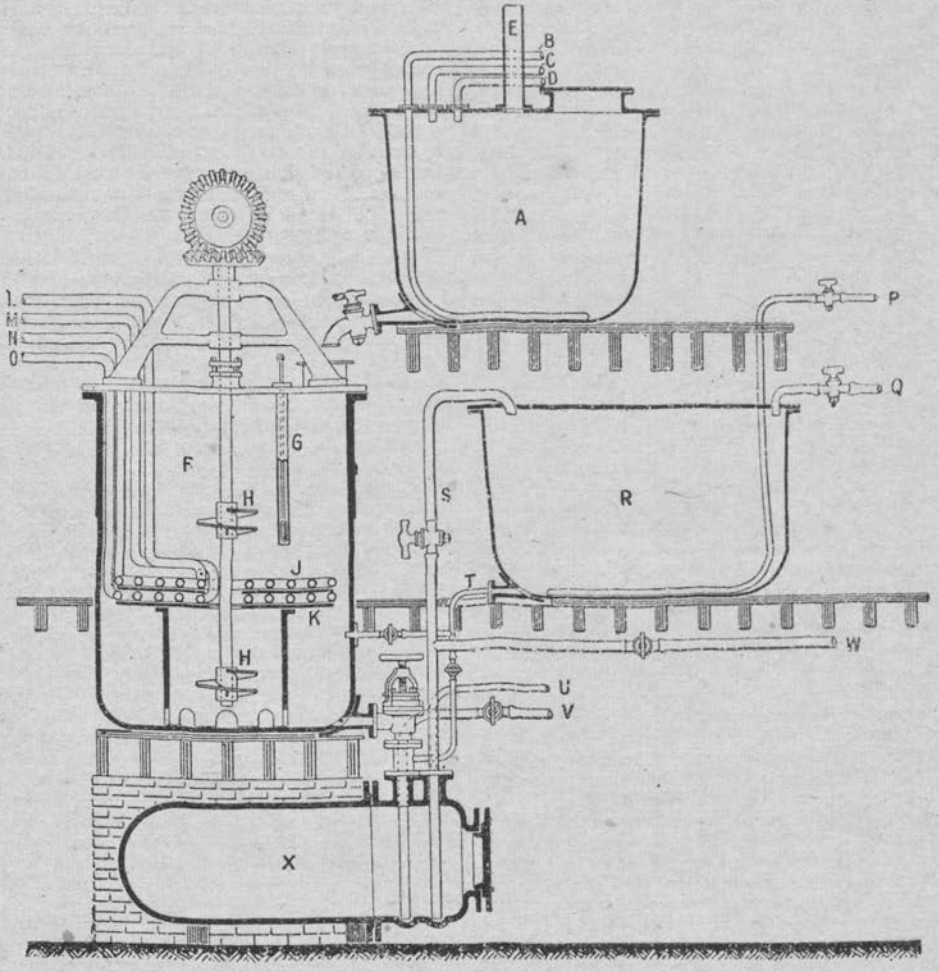


FIG. 4.

A, Mixed-acid pan.
B, Compressed-air pipe.
C, Sulphuric acid inlet.
D, Nitric acid inlet.
E, Acid-vapour pipe.
F, Nitrobenzene pan.
G, Thermometer.
H, Propeller agitator.
J, Lead cooling-coils.
K, Supporting grids.
L, Cooling-water outlet.
M, do. do. do.
N, Cooling-water inlet.
O, Do. do. do.
P, Compressed-air pipe.
Q, Water inlet.
R, Nitrobenzene washpan.
S, Pipe from egg.
T, Nitrobenzene pipe.
U, Compressed-air pipe.
V, Waste-acid pipe.
W, Pipe to N. B. tank.
X, Air-pressure egg.

mixed in the above proportions in large stock tanks. The mixed acid is run in a thin stream into the benzol, while the agitators are revolving at a speed of about 60 revs. per minute. The heat of the reaction is indicated on a long thermometer suspended in a metal tube, which passes through the lid and dips into the liquid. The temperature is kept below 60° by checking the flow of acids if the temperature rises. With a good supply of cooling water passing through the coils, very little attention is required, and the process, which a few years ago was attended with danger and frequent loss, is now carried on almost automatically. This is principally owing to the purity of the benzol employed, and the use of internal cooling coils in place of the outside water-jacket.

It is important that the coils should be of

pure chemical lead, without flaw, and before being used, they should be examined minutely. Some of these coils have been known to work nearly 4 years continuously. The vertical portions, connecting the coils with the exterior, should be protected, as these are quickly attacked. This is done by 'threading' them through lead pipes of slightly larger diameter, and filling up the intervening space with any acid-proof cement. After the full charge of mixed acids has been run into the machine, the agitation is continued for about 4½ hours, and the benzol will then be completely transformed into nitrobenzol. If a sample is then taken while the agitators are running, and allowed to settle, the weak sulphuric (called waste acid) will contain less than 1 p.c. of nitric acid, and the upper layer of nitrobenzol will have a sp.gr. of 1·235. The agitation is then stopped, and the contents of the machine allowed to settle for 5 hours. The 'waste acid,' having settled to the bottom, is run off into the air-pressure egg below, and blown to the sulphuric acid concentrating department to be rectified. The nitrobenzol is next run off into the air-pressure egg and blown into the washing pan above, where it is washed by violent air agitation with an equal volume of water containing sufficient sodium hydroxide to neutralise any trace of acid left in it. After settling a few hours the nitrobenzol settles to the bottom, and is run down into the air-pressure egg, and forced from there into a large store tank, which is set at a high level, so that the contents can run by gravity to the aniline machine. The wash-water, which contains a little nitrobenzol in suspension, is run into a series of settling tanks, and the oil recovered. Although it is possible to work a charge of benzol in each machine daily, it is customary to have a duplicate set of machines, and to work each machine on alternate days. For an output of 150 tons of pure aniline oil per month, six nitrobenzol machines are required, with their corresponding adjuncts, as shown in the figure. The yield of nitrobenzol from the pure benzol employed is 154½ p.c. by weight, and this approaches so near the theoretical yield, viz. 157·6 p.c., that there is little room for improvement. It is possible slightly to increase this yield by settling the waste acid for 48 hours in a series of tanks, and skimming off the nitrobenzol, but in practice it has not been found to pay for the trouble, especially if the previous separation be carefully watched.[1]

When the nitrobenzol is to be sold as 'myrbane,' it is distilled under diminished pressure in order to obtain a perfectly clear and transparent liquid such as the users of myrbane demand. It is customary to use toluene imperfectly freed from benzene for this purpose, that article being cheaper and yielding a somewhat more fragrant myrbane than benzene alone.

The treatment adopted with toluene and xylene is in all essential particulars the same as with benzene. In the former case, however, if the nitrotoluene is not employed direct, the product is separated into *p*- and *o*-nitrotoluene by fractional distillation under diminished pressure through a Savalle column. The distillation is stopped when 40 p.c. has distilled, and the distillate on redistillation gives nearly pure *o*-nitrotoluene (b.p. 233°). The residue on cooling deposits crystals of *p*-nitrotoluene (b.p. 238°; m.p. 54°), which are freed from oil by centrifugating.

(For the estimation of *o*- and *p*-nitrotoluene, *see* Reverdin and De la Harpe, Bull. Soc. chim. 1888, (ii.) 50, 44; Glasmann, Ber. 1903, 36, 4260; Chem. Zeit. 1904, 28, 187; Holleman, Proc. K. Akad. Amsterdam, 1904, 7, 395; Rec. trav. chim. 1908, 27, 458.)

Dinitrobenzene and *dinitrotoluene* are obtained by treating a charge of the hydrocarbon with double the proportion of the mixed acids, the operation being carried out in two stages, and the second charge of acids run in directly after the first. The cooling water is shut off and the temperature allowed to rise rapidly. Or nitrobenzol already manufactured may be taken and again treated with the necessary acid.

The product of the reaction is separated from the acid as usual, and then thoroughly washed with cold, and lastly with hot, water. As dinitrobenzene is sensibly soluble in the latter, the hot wash-water had better always be preserved and used for first washing a subsequent batch. Finally, it is allowed to settle, and, while still warm, run out into iron trays, in which it solidifies in masses 2 to 4 inches thick. The principal product of the reaction is **metadinitrobenzene**, m.p. 89·8°, but **orthodinitrobenzene**, m.p. 118°, and **paradinitrobenzene**, m.p. 172°, are also produced, the m.p. of the commercial product being about 85°–87°. It should not contain any nitrobenzene, and should be well crystallised, hard, and almost odourless, and should not render paper greasy.

Dinitrotoluene is prepared by a process similar to the above, and, since ortho- and para-nitrotoluene yield, when nitrated at a high temperature, most of the 2 : 4-dinitrotoluene, it is better to proceed straight on from the toluene.

The subsequent treatment is the same as when dinitrobenzene is manufactured. Commercial dinitrotoluene consists mainly of the last-named and the 2 : 6- modifications, but always contains small quantities of the other isomerides. The 2 : 6- only occurs in small proportion, and mainly in the oily drainings from the crude product. The nitration of the pure metaxylene does not differ from the processes already described. J. C. C.

BENZENE DIAZONIUM SALTS *v.* DIAZO COMPOUNDS.

BENZIDINE and **BENZIDINE REARRANGEMENT** *v.* DIPHENYL.

BENZIDINE AZO- DYES *v.* AZO- COLOURING MATTERS, and DISAZO- and TETRAZO- COLOURING MATTERS.

BENZIDINE PUCE *v.* AZO- COLOURING MATTERS.

[1] Benzene may also be nitrated by using sodium nitrate instead of nitric acid. A recent recipe is the following: 35 kilos. of benzene and 115 kilos. of sodium nitrate are mixed at 60°–80°, and 150 kilos. of 90–96 p.c. sulphuric acid added slowly. The temperature rises to about 100°, when 65 kilos. of benzene are added, and when the nitration is complete the lower layer of bisulphate is drawn off. The yield is stated to be 150–154 kilos. of washed nitrobenzene, sp.gr. 1·18 at 15°, or 148 kilos. of the pure substance boiling at 96° under a pressure of 18 mm. (Saccharin-fabrik. Akt.-Ges. vorm. Fahlberg, List & Co. D. R. P. 221787, July 21, 1907).

BENZIL *v.* KETONES.

BENZINE, Light petroleum (*v.* PETROLEUM).

BENZO-AURINE, -BLACK BLUE, -BLUE, -BROWNS, -FAST PINK, -FAST SCARLETS, -INDIGO BLUE, -GREY, -OLIVE, -ORANGE, -PURPURINS, -RED BLUE, -VIOLET *v.* AZO-COLOURING MATTERS.

BENZOFLAVINE *v.* ACRIDINE DYESTUFFS.

BENZOIC ACID $C_7H_6O_2$ or $C_6H_5{\cdot}CO_2H$. (*Acide benzoïque*, Fr.; *Benzoësäure*, Ger.) *Acidum benzoicum.* Blaise de Vigenère, in his Traité du feu et du sel, published in 1608, described the preparation of benzoic acid by sublimation from gum benzoïn. Lemery, in 1675, called attention to its acid properties; and Scheele showed, in 1775, that it could be extracted from gum benzoïn by boiling the gum with lime, concentrating the solution, and decomposing the salt with hydrochloric acid. Scheele also, in 1785, obtained benzoic acid from cow's urine; but it was not until 1829 that Liebig showed that the substance contained in the urine, by the decomposition of which benzoic acid is formed, is hippuric acid.

Occurrence.—Benzoic acid occurs in gum benzoïn, tolu balsam, storax, dragon's blood, and various other natural resins; in oil of bergamot and oil of cinnamon; in vanilla, calamus root, and the ripe fruit of the clove tree; in various sweet-smelling flowers—thus in the flowers of *Unona odoratissima*, from which the perfume *ylang-ylang* is prepared; as hippuric acid (and sometimes even, it is asserted, as free benzoic acid) in the urine of herbivora; and in *castoreum*, a viscid, fœtid secretion, found in pouches situated in the perinæum of the beaver.

Formation.—By the oxidation of all compounds which contain the phenyl group united to a single lateral chain, such as toluene, benzyl chloride, benzyl alcohol, benzaldehyde, cinnamic acid, &c. By heating benzotrichloride $C_6H_5{\cdot}CCl_3$ with water. By heating benzonitrile $C_6H_5{\cdot}CN$ with acids or alkalis. By boiling hippuric acid with hydrochloric acid

$$(C_7H_5O)NH{\cdot}CH_2{\cdot}CO_2H+H_2O = C_7H_6O_2+NH_2{\cdot}CH_2{\cdot}CO_2H.$$

By passing carbon dioxide into benzene containing aluminium chloride

$$C_6H_6+CO_2=C_6H_5{\cdot}CO_2H.$$

Preparation.—1. *From gum benzoïn.* In order to obtain the acid from gum benzoïn by sublimation, the gum, broken up into small pieces, is introduced into a flat iron vessel, over the mouth of which filter paper is then pasted. A large conical cap of strong paper, exactly fitting the iron vessel, is placed over the filter paper, tied round the rim, and the whole is gently heated over a sand-bath at a temperature of about 170°. The benzoic acid sublimes through the filter paper and collects in colourless crystals inside the paper cone, from which it is removed at the end of the operation (Mohr, Annalen, 29, 177). The yield is about 4 p.c. of the gum employed, and from three to four hours are required for the sublimation of a pound of benzoic acid. A trace of an aromatic oil from the gum adheres to the crystals, imparting to them a pleasant odour of vanilla, and enhancing their value as a pharmaceutical preparation. On a manufacturing scale a modification of the foregoing laboratory process is employed, in which the gum is heated in a closed vessel and the vapour of the subliming acid flows over into a side chamber and condenses at a point below the source of heat, thus obviating all risk of fusing the sublimate. The gum benzoïn is introduced by means of a metal drawer, which is heated from beneath by gas jets; whilst the sublimed acid collects in a second drawer, and can thus be removed at the end of the operation (comp. Starting, Arch. Pharm. 231, 342). By other methods the yield from gum benzoïn may be increased to 25 p.c.

Wöhler's method (Annalen, 49, 245) consists in dissolving the powdered gum in an equal volume of alcohol of 90–95 p.c., adding fuming hydrochloric acid to the hot solution until a precipitate begins to be formed, and distilling the mixture. The distillate contains ethyl benzoate, alcohol, and hydrochloric acid. The residue is again distilled with water as long as ethyl benzoate passes over, and the united distillates are boiled with caustic potash to decompose the ethyl benzoate. From the solution the benzoic acid is precipitated with hydrochloric acid. It smells like the sublimed product.

Scheele's method of extracting the benzoic acid from the gum with slaked lime and water (*v. supra*), may also be employed.

2. *From urine.* The urine of the cow or horse is allowed to putrefy, so as to induce a hydrolytic decomposition of the hippuric acid into benzoic acid and glycocoll. Milk of lime is then added, the filtered solution is evaporated to a small bulk, and the benzoic acid precipitated with hydrochloric acid. In order to avoid the evaporation and the attendant disagreeable smell, the excess of lime may be removed by carbon dioxide, the benzoic acid precipitated by the addition of ferric chloride, and the ferric benzoate, after separating it by filtration, decomposed by hydrochloric acid. The acid thus prepared smells of urine, and must not be used in medicine. The smell may, however, be removed or concealed by mixing the acid with a small quantity of gum benzoïn and subliming it.

The fresh urine may also be evaporated to one-third of its bulk, filtered, mixed with hydrochloric acid, and allowed to cool. Hippuric acid crystallises out, which, by boiling with concentrated hydrochloric acid, is decomposed into glycocoll hydrochloride and benzoic acid. Benzoic acid may also be prepared by the action of ammonia and zinc-dust on gallic acid and catechu-tannic acid (Guignet, Compt. rend. 113, 200).

3. *From toluene.* Most of the benzoic acid employed at the present day, and certainly all that is employed in the coal-tar colour industry, is manufactured from toluene (*v. infra*). Toluene by oxidation with nitric acid, may be directly converted into benzoic acid; but it is better to chlorinate it first to benzyl chloride, which is more readily attacked by the oxidising agent. Lunge and Petri (Ber. 10, 1275) boil benzyl chloride (1 part) and dilute nitric acid (3 parts of acid of 35°Baumé with 2 parts of water) in a reflux apparatus until the smell of benzyl chloride and benzaldehyde is no longer perceptible. A. v. Rad (Dingl. poly. J. 231, 538), however, states that this method is unsuited for preparing the acid on a manufacturing scale, and

prefers to decompose benzotrichloride by heating it with water under pressure:

$$C_6H_5{\cdot}CCl_3+2H_2O=C_6H_5{\cdot}CO_2H+3HCl;$$

but it is difficult to prepare pure benzotrichloride, and the benzoic acid manufactured by this process is always contaminated with chlorobenzoic acids formed from chlorinated benzotrichlorides.

Espenschied (D. R. P. 47187) boils the benzotrichloride with milk of lime, or with a solution of caustic soda mixed with whiting or other insoluble matter, the presence of which aids the reaction by preventing the benzotrichloride from forming a separate layer and also by promoting local superheating.

E. Jacobsen (D. R. P. 11494 and 13127) heats benzotrichloride with acetic acid to which a little zinc chloride has been added:

$$C_6H_5{\cdot}CCl_3+2CH_3{\cdot}CO_2H=C_6H_5{\cdot}CO_2H+2CH_3{\cdot}COCl+HCl$$

The acetyl chloride is distilled off, the residue extracted with sodium carbonate, and the benzoic acid precipitated with hydrochloric acid.

The benzoic acid required in the coal-tar colour industry is obtained as a by-product in the manufacture of benzaldehyde by heating benzal chloride with milk of lime (*v.* BENZALDEHYDE), a portion of the benzaldehyde being converted into calcium benzoate in this process.

4. *From coal-tar oil.* Aktiengesellschaft für Theer und Erdöl Industrie, Eng. Pat. 7867; D. R. P. 109122; J. Soc. Chem. Ind. 1899, 785. The carbolic or creosote oil fraction, obtained from coal tar, and boiling between 160° and 240°, contains benzonitrile. The fraction from which phenol is obtained is washed with dilute soda lye (sp.gr. 1·1) to remove the phenol and cresol, and the remaining oil placed in a jacketed vessel, provided with an agitator and connected with a condenser and receiver. Caustic soda lye (sp.gr. 1·4) is added in about twice the quantity corresponding to the benzonitrile present. The mixture is agitated, and wet steam passed in for some hours, as long as ammonia is evolved in considerable quantity. The receiver then contains the lower boiling constituents of the oil, together with a somewhat concentrated ammonia solution, whilst the contents of the still consist of a lower alkaline layer and an upper oily one. The former is neutralised with carbonic acid or a mineral acid, separated from traces of phenol or resinous matters, and the resulting solution of sodium benzoate decomposed whilst hot by adding an excess of acid. On cooling, pure benzoic acid separates in white crystals.

5. *From the naphthols and other naphthalene derivatives.* Basle Chemical Works, J. Soc. Chem. Ind. 1901, 1139; D. R. P. 136410; Fr. Pat. 313187; Eng. Pat. 15527; U.S. Pat. 702171. (*See also* Chem. Zentr. 1903, i. 546, 857, 1106; D. R. PP. 138790, 139956, 140999.) By heating the naphthols or other naphthalene derivatives to about 250°, in presence of alkali with metallic oxides or peroxides such as copper or iron oxide, barium, lead or manganese peroxide, they yield phthalic and benzoic acids, and a few intermediate products. The excess of alkali is removed by lixiviation with a little water; the acids are then dissolved in water and decanted from the reduced oxide. This solution is saturated with carbon dioxide and filtered from unchanged naphthol. The filtrate is decomposed with sulphuric acid and evaporated, the precipitated acids being purified by distillation.

6. *By the electrolytic oxidation of phenanthrene.* Farbwerke vorm. Meister, Lucius and Brüning, Chem. Zentr. 1904, ii. 71; D. R. P. 152063.

Properties.—It crystallises in lustrous leaflets or flat needles of sp.gr. 1·2659 15°/4°, melting at 121·4°. It boils at 249°, but is volatile even at 100°, so that it may readily be sublimed; the vapour excites coughing. It may be distilled with steam; 2 litres of aqueous distillate contain 1 gram of benzoic acid. 1000 parts of water dissolve at

0°	20°	40°	60°	80°	100°
1·70	2·90	5·55	11·55	27·15	58·75

(Bourgoin, Arch. Pharm. [5] 15, 168); it is soluble in about twice its weight of ether and in about its own weight of absolute alcohol at ordinary temperatures.

Traces of impurity lower the melting-point of benzoic acid very considerably. The impure acid is also deposited from its solutions in smaller crystals than the pure.

(For *absorption spectra, see* Hartley and Headley, Chem. Soc. Trans. 1907, 319.)

Reactions.—When heated with *lime*, benzoic acid yields benzene and calcium carbonate (Mitscherlich). It is very stable towards oxidising agents; dilute *chromic acid* is without action on it, but by warming it with *manganese dioxide and sulphuric acid* it is converted into formic acid, carbon dioxide, and phthalic acid—the latter being formed by the simultaneous oxidation of formic and benzoic acids (Carius, Annalen, 148, 72). *Sodium amalgam* reduces benzoic acid in boiling alcoholic solution to benzyl alcohol, benzaldehyde, and tetrahydrobenzoic acid (Aschan, Ber. 24, 1864, and Annalen, 271, 231). By electrolytic reduction, benzaldehyde is obtained (Mettler, Ber. 41, 4148), and by reduction with hydrogen and platinum, hexahydrobenzoic acid is the chief product (Willstätter and Mayer, Ber. 41, 1479). When distilled over heated *zinc-dust* it yields benzaldehyde (Baeyer, Annalen, 140, 296). Calcium benzoate yields on distillation benzophenone $C_6H_5{\cdot}CO{\cdot}C_6H_5$, together with a small quantity of benzene and anthraquinone $C_{14}H_8O_2$ (Kekulé and Franchimont, Ber. 5, 908). Taken internally, benzoic acid is excreted in the urine as hippuric acid (Wöhler).

When a solution of ferric chloride which has been mixed with sufficient ammonia to turn it dark-red is added to a solution of a benzoate, a flesh-coloured precipitate of basic ferric benzoate $(C_7H_5O_2)_3Fe,Fe(OH)_3$ is formed. This reaction is used in the separation of benzoic acid, and also in separating iron from manganese.

Uses.—Benzoic acid is used in medicine; but for this purpose only the natural product, obtained from gum benzoïn by sublimation, is suitable. Adulteration with the artificial acid is detected by heating a portion of the acid on platinum wire and holding a porcelain dish moistened with phloroglucolvanillin over the flame; the production of a red colour, due to the presence of hydrochloric acid, indicates the presence of the artificial acid. Artificial benzoic acid is employed in the manufacture of aniline

blue. It has been used as a mordant in calico-printing. Benzoic acid, dissolved in a mixture of 1 part of ether and 20 parts of alcohol, has been recommended for the preservation of anatomical preparations. It is said to be used in giving an aroma to tobacco.

As an antiseptic it is injurious to health, producing serious disturbance of the metabolic functions, attended with injury to the digestion (Wiley, U.S. Dept. of Agric., J. Soc. Chem. Ind. 1908, 914).

Detection in foodstuffs.—By the production of diaminobenzoic acid (Mohler, Bull. Soc. chim. 3, 414); by the action of the acid on rosaniline hydrochloride dissolved in aniline oil, when aniline blue is formed (De Brevans, J. Pharm. Chim. 14, 438); by converting the acid into salicylic acid with hydrogen peroxide, and then adding ferric chloride (Jonescu, J. Pharm. Chim. 29, 523). *In butter*: By the formation of ammonium diaminobenzoate, which gives a brownish-red colouration in alkaline solution (Halphen, Pharm. J. 28, 201; Robin, Ann. Chim. anal. 14, 53). *In fermented beverages and milk*: As in butter (Robin, Ann. Chim. anal. 14, 53; Breustedt, Arch. Pharm. 237, 170). *In meats and fats* (Fischer and Gruenert, J. Soc. Chem. Ind. 28, 849).

Examination of the commercial product.—The artificial benzoic acid of commerce is almost always contaminated with chlorobenzoic acids (*v. supra*), the presence of which in any considerable quantity is stated to be detrimental in the aniline blue manufacture. The chlorine may be detected by heating the acid with metallic sodium, extracting the residue with water and testing the solution with silver nitrate. The acid should have the proper melting-point, and should dissolve without residue in boiling water.

Salts and esters of benzoic acids. Benzoic acid is monobasic. Most of the benzoates are soluble both in water and in alcohol. *Potassium benzoate* $C_7H_5O_2K,3H_2O$: efflorescent laminæ. *Sodium benzoate* $C_7H_5O_2Na,H_2O$: efflorescent needles, used for inhalation in tuberculosis. *Ammonium benzoate* $C_7H_5O_2(NH_4)$, rhombic crystals, also used in medicine. *Calcium benzoate* $(C_7H_5O_2)Ca,2H_2O$, lustrous needles, used in the preparation of benzophenone. *Basic ferric benzoate* $(C_7H_5O_2)_3Fe,Fe(OH)_3$ (*v. supra*). *Mercuric benzoate* small white odourless tasteless crystals; powerful antiseptic; successfully employed in syphilitic and similar diseases (Merck's Bull. 1890, [5] 33; [6] 49; [7] 73).

The esters of benzoic acid are obtained either by distilling benzoic acid with the alcohol and sulphuric acid, or better, by saturating a solution of benzoic acid in the alcohol with hydrogen chloride, digesting the mixture on the water-bath for some hours, precipitating the ester with water, and purifying by distillation. *Methyl benzoate* $C_7H_5O_2{\cdot}CH_3$ is a liquid boiling at 198·6° (Perkin, Chem. Soc. Trans. 69, 1025). *Ethyl benzoate* $C_7H_5O_2{\cdot}C_2H_5$, boils at 211·8° (Perkin, *l.c.*). *Propyl benzoate* $C_7H_5O_2{\cdot}C_3H_7$, boils at 230·7° (Perkin, *l.c.*).

Benzyl benzoate. This ester forms the therapeutically active portion of Peru balsam, and also the larger fraction of the product formerly known by the name of *cinnameïn*, and generally described as consisting chiefly or entirely of benzyl cinnamate. Benzyl benzoate is a colourless oil, boiling at 173° under 9 mm. pressure, whilst the benzyl cinnamate is crystalline, melting at 37°, and boiling at 213°–214° under 9 mm. pressure. It is stated that benzyl benzoate is as efficacious, therapeutically, as the ester obtained direct from Peru balsam, whilst it has the advantages that it is free from colour and smell, is constant in composition, and does not cause the irritation sometimes occasioned by Peru balsam owing to the free acids present (E. Erdmann, Pharm. J. 65, 387).

BENZOIC ANHYDRIDE $(C_6H_5{\cdot}CO)_2O$. First prepared by Gerhardt (Ann. Chim. Phys. [3] 37, 299) by the action of benzoyl chloride on sodium benzoate or on sodium oxalate, or of phosphorus oxychloride on sodium benzoate:

$$C_6H_5{\cdot}CO_2Na+C_6H_5{\cdot}COCl=(C_6H_5{\cdot}CO)_2O+NaCl;$$

$$2C_6H_5{\cdot}COCl+Na_2C_2O_4=(C_6H_5{\cdot}CO)_2O+2NaCl+CO+CO_2;$$

$$4C_6H_5{\cdot}CO_2Na+POCl_3=2(C_6H_5{\cdot}CO)_2O+NaPO_3+3NaCl.$$

Preparation.—Pour 100 grams of phosphorus oxychloride over 500 grams of dry sodium benzoate contained in a flask; complete the reaction by heating at 150°; remove sodium salts by washing the cooled mass with dilute sodium carbonate, and purify the anhydride by distillation.

Anschütz (Annalen, 226, 15) heats benzoyl chloride with anhydrous oxalic acid. This avoids the formation of metallic salts altogether.

It may also be prepared by heating benzoyl chloride with fused and powdered sodium nitrite for 12 hours; the product is extracted with ether and freed from traces of benzoic acid by rapidly washing with a very dilute solution of sodium carbonate, and finally with distilled water; yield 70 p.c. (Minunni and Caberti, Gazz. chim. ital. 20, 655). By mixing together benzoyl chloride and pyridine and adding water after half an hour, pure benzoic anhydride is precipitated; yield 80 p.c. (Minunni, Gazz. chim. ital. 22, ii. 213). By treating benzoyl chloride with sodium carbonate and pyridine; yield quantitative (Deninger, J. pr. Chem. 50, ii. 479). By treating benzoyl chloride with sodium hyposulphite in the presence or absence of pyridine (Binz and Marx, Ber. 40, 3855); by treating benzenesulphonic chloride with sodium benzoate (Chem. Fab. von Heyden, D. R. P. 123052; Chem. Zentr. 1902, 2, 518); by treating benzoic acid or sodium benzoate with methylchlorsulphate (Bad. Anil. and Sod. Fabrik, D. R. P. 146690; Chem. Zentr. 1904, i. 65); by treating benzoic acid with acetic anhydride in the presence of an indifferent solvent such as benzene or xylene (Kaufmann and Luterbacher, Ber. 42, 3483); from benzotrichloride and acetic acid (Béhal, Compt. rend. 148, 648).

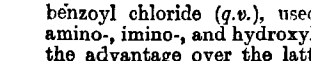
Properties.—Rhombic prisms, sp.gr. 1·1989 15°/4°, melting at 42°, and boiling at 360° (corr.) (Lumsden, Chem. Soc. Trans. 1905, 93). Insoluble in water; readily soluble in alcohol and ether.

Reactions.—Water decomposes it very slowly in the cold, more rapidly on boiling, with formation of benzoic acid. Towards ammonia, amino- and imino- compounds, alcohols and phenols, it behaves like benzoyl chloride, replacing by a benzoyl- group a hydrogen atom attached to nitrogen or oxygen. For this reason it is, like

benzoyl chloride (*q.v.*), used as a reagent for amino-, imino-, and hydroxyl- groups, and it has the advantage over the latter reagent that no hydrochloric acid, a substance which has a very prejudicial effect on many organic compounds, is liberated during its action.

BENZOÏN GUM *v.* BALSAMS.

BENZOÏN YELLOW. This compound is obtained by condensing benzoïn with gallic acid. Benzoïn is added to a solution of gallic acid in sulphuric acid, kept at a temperature of 0°–5°, and, after being stirred during 24 hours, the mixture is poured into water, the dye being precipitated. It crystallises from a mixture of acetic acid and alcohol in yellow needles. Its constitution is given as



[O:$(OH)_2$:CO=1:2:3:4]

(Bad. Anil. Sod. Fab. D. R. P. 95739; Chem. Zentr. 1898, i. 870, and Graebe, Ber. 31, 2975) (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

BENZONAPHTHOL *v.* SYNTHETIC DRUGS.

BENZOPHENONE (*Diphenyl Ketone*) (*v.* KETONES).

BENZOSALIN. Trade name for benzoyl-salicylic-acid-methyl ester, used in the treatment of articular and muscular rheumatism, neuritis, neuralgia, and sciatica. *V.* SYNTHETIC DRUGS.

BENZOSOL *v.* SYNTHETIC DRUGS.

BENZOTRICHLORIDE *v.* TOLUENE, CHLORINE DERIVATIVES OF.

BENZOYL CHLORIDE $C_6H_5{\cdot}COCl$. First obtained by Liebig and Wöhler, by passing chlorine into benzaldehyde (Annalen, 3, 262). By the action of phosphorus pentachloride on benzoic acid (Cahours, Ann. Chim. Phys. [3] 23, 334).

Preparation.—Benzoic acid is heated with slightly more than the molecular proportion of phosphorus pentachloride

$$C_6H_5{\cdot}COOH+PCl_5=C_6H_5{\cdot}COCl+POCl_3+HCl.$$

The resulting benzoyl chloride is freed from the phosphorus oxychloride by fractional distillation. Commercial benzoyl chloride is usually contaminated with chlorbenzoylchloride and frequently with small quantities of benzaldehyde (V. Meyer, Ber. 24, 4251, and 25, 209).

From oxalyl chloride, benzene, and aluminium chloride (Staudinger, Ber. 1908, 3566). From benzoic acid or sodium benzoate and methylchlorosulphate (Bad. Anil. and Sod. Fabrik, D. R. P. 146690; Chem. Zentr. 1904, i. 65).

From salts of benzoic acid. By treatment with sulphur dioxide and chlorine (Farb. vorm. Meister, Lucius and Brüning, D. R. P. 210805; Chem. Zentr. 1909, 279).

Properties.—Colourless liquid, with a pungent odour, boiling at 199° (Lumsden, Chem. Soc. Trans. 1905, 94); 197·2° (corr.) (Perkin, Chem. Soc. Trans. 69, 1244). Its vapour attacks the eyes, causing a flow of tears. Sp.gr. 1·2122 20°/4° (Brühl, Annalen, 235, 11).

Reactions.—Benzoyl chloride reacts with *water*, slowly in the cold, rapidly on heating, with formation of benzoic and hydrochloric acids. With *ammonia* it forms benzamide

$$C_6H_5{\cdot}CO{\cdot}NH_2$$

together with ammonium chloride. In like manner it reacts with compounds containing hydroxyl-, amino-, or imino- groups, introducing benzoyl in place of hydrogen, and is therefore employed in organic chemistry as a test for the presence of these groups in a compound. Thus with *alcohol* it yields ethyl benzoate; with *aniline*, benzanilide and dibenzanilide.

BENZOYL GLYCOCOLL *v.* HIPPURIC ACID.

BENZOYL PINK *v.* AZO- COLOURING MATTERS.

BENZOYL SULPHONIC IMIDE and **BENZOIC SULPHINIDE** *v.* SACCHARIN.

BENZYLAMINE CARBOXYLIC ACIDS *v.* AMINO- ACIDS (aromatic).

BENZYL BLUE. A dye made by the Aktiengesellschaft für Anilinfabrikation, Berlin, by substituting three atoms of hydrogen in rosaniline by three benzyl- groups. It is easily soluble, in water; dyes silks, wools, and cotton (Reimann's Färber-Zeit, 1879, 251; Industrie-Blätter, 39, 360).

BENZYL CHLORIDE *v.* TOLUENE, CHLORINE DERIVATIVES OF.

BENZYLDIPHENYLAMINE *v.* DIPHENYLAMINE.

BENZYLPHENYLHYDRAZONES *v.* HYDRAZONES.

BERBERINE *v.* BARBERRY ROOT and VEGETO-ALKALOIDS.

BERENGELITE. A bituminous resinous mineral from St. Juan de Berengela, Peru, melting at 100°, soluble in alcohol and ether. According to Dietrich, specimens from Trinidad and Arien, Peru, contained 71·84 C, 9·95 H, and 18·21 of O (Chem. Zentr. 80, 559). Used for caulking ships.

BERGAMOT *v.* OILS, ESSENTIAL.

BERGMANN'S POWDER. An explosive composed of 50 parts potassium chlorate, 5 of pyrolusite, and 45 of bran, sawdust, or tan (J. 37, 1748).

BERLIN BLACK. A black varnish drying with a dead surface, used for coating iron-work.

BERLIN BLUE or **PRUSSIAN BLUE** *v.* CYANIDES.

BERNTHSEN'S VIOLET. *Isothionine. β-Amidothiodiphenylimide.* Formed by reducing β-dinitrodiphenylaminesulphoxide and oxidising the leuco- base with ferric chloride. The hydrochloride crystallises in needles. Dyes reddish-violet. Isomeric with *Lauth's violet* (Bernthsen, Annalen, 230, 133).

BERRY WAX *v.* WAXES.

BERTHIERITE. *Iron sulphantimonite* (*v.* ANTIMONY).

BERYL. A mineral consisting of glucinum aluminium silicate $Be_3Al_2Si_6O_{18}$, crystallising in the hexagonal system. The ancient name, *βήρυλλος*, included also some other gem-stones of a greenish colour. The crystals are usually quite simple in form, with only the hexagonal prism and the basal plane; the habit being commonly prismatic and the prism faces striated vertically. They are usually cloudy or opaque, with a pale-greenish or yellowish colour and are often of considerable size, crystals weighing as much as one or two tons having been found at Acworth in New Hampshire. The sp.gr. is 2·63–2·80, and the hardness 7½–8. The material is not attacked by acids, except hydrofluoric; and before the blowpipe is fusible only with difficulty on the edges.

Crystals of a different type are found in association with lithia minerals (lepidolite and rubellite) in certain pegmatites. These are tabular in habit and rose-red or colourless. Further, they differ chemically in containing small amounts of alkalis (Cs_2O 3·1, Li_2O 1·4 p.c.). V. Vernadsky (1908) expresses the composition by the formula $xBeAl_2Si_4O_{12}{\cdot}yA$, where A is BeH_2SiO_4, $BeSiO_3$(?), Cs_2SiO_3, Li_2SiO_3, or Na_2SiO_3; and for the cæsium-bearing variety he proposes the name *vorobyevite*.

Being by far the most abundant of glucinum minerals, beryl is employed for the preparation of the little-used salts of glucinum. It finds more extensive application in jewellery. The clear grass-green variety is the *emerald*, one of the most valuable of gems on account of the rarity of flawless material. Gem-stones of a greenish, bluish, or sea-green colour are known as *aquamarine*, while others are golden-yellow or rose-pink. L. J. S.

BERYLLIUM *v.* GLUCINUM.

BERZELIANITE. Native copper selenide Cu_2Se, occurring in a black powdery form in calcite at Skrikerum in Sweden and at Lehrbach in the Harz. Named after the Swedish chemist J. J. Berzelius (1779–1848), who first analysed it. L. J. S.

BERZELIITE. Arsenate of calcium, manganese, and magnesium $(Ca,Mn,Mg)_3As_2O_8$, occurring as small yellow cubic crystals, and as compact masses, with ores of iron and manganese at Långban in Wermland, Sweden. Also named after J. J. Berzelius. Other forms of the same name, berzeline and berzelite, have been applied to these, as well as to some other minerals. L. J. S.

BESSEMER STEEL *v.* IRON.

BETAINE $(CH_3)_3N\langle\begin{matrix}CH_2\\O\end{matrix}\rangle CO$ may be regarded as the internal anhydride of the acid $(CH_3)_3N(OH){\cdot}CH_2{\cdot}COOH$ derived from acetic acid by the replacement of one atom of hydrogen by trimethyl hydroxyammonium. It occurs in beets and mangolds (especially unripe roots), in cotton seed, in the shoots of barley, in wormseed (*Artemisia gallica*) and in many other plants, often in association with choline, from which it may readily be obtained by oxidation.

Betaine can be synthesised by the interaction of chloracetic acid and trimethylamine (Liebreich, Ber. 1869, 2, 13).

It can be extracted from beet-root molasses by dilution with water, boiling with baryta, filtering, precipitating the excess of BaH_2O_2 with CO_2, evaporating the liquid to small volume, and extracting with alcohol. The alcoholic solution is treated with alcoholic zinc chloride, the ppt. recrystallised from water and decomposed by baryta water. The barium is then exactly removed from the filtrate by H_2SO_4, and betaine hydrochloride crystallises on evaporation (Liebreich, Ber. 3, 161; Frühling and Schulz, Ber. 10, 1070).

A general method of obtaining betaine from plant extracts is to precipitate with lead acetate, filter, remove the lead by sulphuretted hydrogen, filter, evaporate to dryness, extract residue with alcohol, and precipitate with alcoholic mercuric chloride. The mercuric double salt is then recrystallised, decomposed by sulphuretted hydrogen, and the hydrochloride obtained from the solution by evaporation. If choline is also present, it can be removed from the mixed hydrochlorides by extraction with cold alcohol, leaving the betaine hydrochloride (Schulze, Zeitsch. physiol. Chem. 1909, 60, 155).

Betaine crystallises from alcohol in large crystals containing one molecule of water. It is deliquescent in air, and loses its water when dried over sulphuric acid. Strong sulphuric acid has but little action upon it, even at 120° (Stanék, Zeit. Zuckerind, Böhm, 1902, 26, 287).

It is neutral to litmus, and has a sweet taste. It melts and decomposes at 293° (Willstätter, Ber. 1902, 35, 584), giving off the smell of trimethylamine and of burnt sugar. The aurichloride $C_5H_{11}NO_2{\cdot}HCl{\cdot}AuCl_4$, forms plates or needles which melt at 209° (Willstätter), or, according to Fischer (Ber. 1902, 35, 1593), at 250°. The platinichloride $PtCl_4{2}(C_5H_{11}NO_2,HCl){\cdot}4H_2O$ forms large plates; after losing its water it melts and decomposes at 242° (Willstätter).

$C_5H_{11}NO_2{\cdot}HCl$ is very soluble in water, slightly soluble in cold alcohol. $C_5H_{11}NO_2{\cdot}HI$ is soluble in water or boiling alcohol, and melts at 188°–190°. A compound with KI crystallises as $(C_5H_{11}NO_2)_2{\cdot}KI,2H_2O$, m.p. 139° (Korner and Menozzi, Gazz. chim. ital. 13, 351), or, if anhydrous, at 228°–229° (Willstätter).

The term 'betaine' is now used generally for substances containing the group

$$\equiv N\langle\begin{matrix}CH_2-\\O-CO-\end{matrix}$$

with other alkyl- groups than methyl, or other acyl- groups than acetyl.

Thus, *dimethylethylacetylbetaine* or (since acetyl is to be understood if no acyl- group is mentioned) *dimethylethylbetaine*

$$(CH_3)_2(C_2H_5)N\langle\begin{matrix}CH_2\\O\end{matrix}\rangle CO$$

crystallises from alcohol in four-sided plates, melting and decomposing at 229°–231° (Willstätter), while *trimethylbutyrobetaine*

$$(CH_3)_3N\langle\begin{matrix}CH_2-CH_2-CH_2\\O\end{matrix}\rangle CO$$

crystallises in colourless plates with $3H_2O$; in the anhydrous state it softens at 130° and decomposes at 222° (Willstätter).

The betaines are isomeric with the esters of amino- acids; thus, ordinary betaine is isomeric with methyldimethylaminoacetate $(CH_3)_2N{\cdot}CH_2{\cdot}CO{\cdot}OCH_3$, a volatile oily liquid, b.p. 135°, while trimethylbutyrobetaine is isomeric with methyl-γ-dimethylaminobutyrate $(CH_3)_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COO{\cdot}CH_3$, b.p. 171°–173°.

(For betaines of the pyridine series, *see* Kirpal, Monatsh. 1908, 29, 471.)

According to Schulze and Trier (Zeitsch. physiol. Chem. 1910, 67, 46), the three betaines which have been isolated from plant tissues are: betaine, trigonelline [found in fenugreek by Jahns (Ber. 1886, 18, 2518) associated with choline], and stachydrine, found in the tubers of *Stachys tuberifera* and in the leaves of *Citrus aurantium* (*v.* TRIGONELLINE and STACHYDRINE). H. I.

BETEL. A mixture of the leaf of the betel-pepper, *Piper Betle* (Linn.) with the fruit of *Areca catechu* (Linn.) or betel nut and *chunam* (lime obtained by calcining shells), universally

used by the people of Centra land Tropical Asia as a masticatory.

BETEL-NUT. The fruit of *Areca catechu* (Linn.).

BETH-A-BARRA WOOD. A wood imported from the West Coast of Africa, much valued for its toughness and capability of receiving a high polish. The interstices of the fibres are filled with a yellow crystalline substance which can be extracted from the sawdust by heating with distilled water containing a little sodium carbonate, and precipitating the resulting claret-coloured solution with acetic acid. It is purified by repeated crystallisations from 80 p.c. alcohol. By precipitating the red solution with hydrochloric acid and washing the resulting precipitate with ether, Greene and Hooker (Amer. Chem. J. 11, 267) found the crystals to be identical in all respects with lapachic acid.

If differs from chrysophanic acid by melting at 135° and in not forming a compound with alum (Sadtler a. Rowland, Amer Chem. J. 1881, 22). (For tables showing the difference in the reactions of brasilin, hæmatoxylin, santalin, and beth-a-barra, *v.* Amer. Chem. J. 11, 49, and Wagner's Jahr. 28, 537.)

BETOL *v.* SYNTHETIC DRUGS.

BETORCIN or **β-ORCIN** $C_8H_{10}O_2$. A substance obtained by the decomposition of barbatic acid, found in the lichen *Usnea barbata*. It is less soluble in water than orcin, and gives a deeper crimson colour with hypochlorites. Kostanecki has obtained it by the action of nitrous acid on *m*-amino-*p*-xylenol, thus showing that it is a dihydroxy-xylene (dimethylresorcinol) having the substituting groups in the positions CH_3, CH_3, OH, OH=1, 4, 3, 5 (Stenhouse a. Groves, Chem. Soc. Trans. 37, 396; Lampartie, Annalen, 134, 248; Menschutkin, Bull. Soc. chim. 2, 428; Kostanecki, Ber. 19, 2321).

BETULA RESIN *v.* RESINS.

BEZETTA. *Tournesol en drapeaux. Schminklappchen. Bezetta rubra et cærulea.* A dye or pigment prepared by dipping linen rags in solutions of certain colouring matters. Red bezetta is coloured with cochineal, and is used as a cosmetic.

Blue bezetta (*Tournesol en drapeaux*), which is chiefly used for colouring the rind of Dutch cheeses, is prepared at Gallargues, near Nîmes, in the department of Gard, from a euphorbiaceous plant, *Chrozophora tinctoria* (A. Juss.) [*Croton tinctorius*]. The fruits and the tops of the plants are gathered, and, the juice being expressed, rags of coarse cloth are dipped into it, then dried, and afterwards exposed to the fumes of mules' or horses' dung. This last operation is called *aluminadou*. The cloths are turned from time to time, to ensure uniform colouration and prevent any part from being exposed too long to the fumes of the dung, which would turn them yellow. They are then dried a second time, again soaked in the juice, mixed this time with urine, and lastly exposed for some time to the action of the sun and wind. The quantity thus manufactured amounts to about 50 tons yearly. The blue of bezetta is reddened by acids like litmus, though not so quickly, but differs from the latter in not being restored by alkalis. According to Joly, the same dye may be obtained from other euphorbiaceous plants, *Chrozorphora oblongata* [*obliqua* (A. Juss.) ?], *C. plicata* (A. Juss.), *Argithamnia tricuspidata* (Muell.), *Mercurialis perennis* (Linn.), and *M. tomentosa* (Linn.). The juice exists in all these plants in the colourless state, and turns blue only on exposure to the air (Handw. d. Chem. 2, [1] 1030; Gerh. Traité, 3, 820).

BEZOAR. This name, which is derived from a Persian word signifying an antidote to poison, was given to a concretion found in the stomach or intestines of an animal of the goat kind, *Capra aegragus*, which was once very highly valued for this imaginary quality, and has thence been extended to all concretions found in animals.

According to Taylor (Phil. Mag. No. 186, 36, and No. 186, 192), bezoars may be divided into nine varieties: 1. Phosphate of calcium, which forms concretions in the intestines of many mammalia. 2. Phosphate of magnesium; semi-transparent and yellowish, and of sp.gr. 2·160. 3. Phosphate of ammonium and magnesium; a concretion of a grey or brown colour, composed of radiations from a centre. 4. Oxalate of calcium. 5. Vegetable fibres. 6. Animal hair. 7. Ambergris. 8. Lithofellic acid. 9. Ellagic or bezoardic acid.

Of true bezoars there are three kinds: Oriental, Occidental, and German. The true Oriental bezoars found in the *Capra ægragus*, the gazelle (*Gazella dorcas*), and other ruminant animals, are spherical or oval masses, varying from the size of a pea to that of the fist, and composed of concentric layers of resinous matter with a nucleus of some foreign substance, such as pieces of bark or other hard vegetable matter which the animal has swallowed. They have a shining resinous fracture, are destitute of taste and odour, nearly insoluble in water and aqueous hydrochloric acid, but soluble for the greater part in potash lye. These characters suffice to distinguish the Oriental bezoars from those varieties which contain a considerable quantity of inorganic matter. There are two kinds of them, the one consisting of ellagic, the other of lithofellic acid. The latter have a more waxy lustre and greener colour than the former, and are also distinguished by their lower sp.gr., viz. 1·1, whilst that of the ellagic acid stones is 1·6. They contain, besides lithofellic acid, a substance resembling the colouring matter of bile, and are perhaps biliary calculi. Oriental bezoars are greatly prized in Persia and other countries of the East for their supposed medical properties. The Shah of Persia sent one in 1808 as a present to Napoleon. The Occidental bezoars are found in the lama (*Auchenia glama*) and in *A. vicugna*. They resemble the Oriental in external appearance, but differ totally in their chemical characters, inasmuch as they consist chiefly of calcium phosphate, with but little organic matter. German bezoars, which are chiefly obtained from the chamois or gemsbock (*Rupicapra tragus*), consist chiefly of interlaced vegetable fibres or animal hairs bound together by a leathery coating.

BICUHYBA FAT. *See* MYRISTICA FAT GROUP.

BIDRY. An Indian alloy of zinc, copper, and lead, and occasionally tin. Articles of this alloy, after being turned in a lathe and engraved, are blackened by immersion in a solution of sal ammoniac, nitre, common salt, and copper sulphate. Known also as *Vidry*.

BIEBRICH ACID RED, PATENT BLACKS, SCARLET PONCEAU *v.* AZO- COLOURING MATTERS.

BILBERRY. *Vaccinium Myrtillus* (Linn.). König gives as the average composition of the fruit:

Water	Protein	Free acid	Sugar	Other carbo-hydrates	Crude fibre	Ash
78·4	0·8	1·7	5·0	0·9	12·3	1·0

According to Otto (Bied. Zentr. 1899, 28, 284), Silesian bilberries contain from 3·5 to 7·0 p.c. of sugar and acid corresponding to from 0·9 to 1·5 p.c. of tartaric acid. He found that fermentation of the juice with ordinary yeast was very slow unless some nitrogenous matter (*e.g.* ammonium chloride or, better, asparagine (about 0·6 gram per litre)) were added. Bilberries contain a small quantity of a wax melting at 71° (Seifert, Landw. Versuchs-Stat. 1894, 45, 29).

The juice of bilberries contains from 4 to 9·5 p.c. of total solids, 0·25 to 0·31 p.c. ash, and acidity corresponding to from 15·5 to 19·6 c.c. N/1 alkali. The juice contains some substance which gives a blue colouration when heated with hydrochloric acid. This colouration is apparently not connected with the red colouring matter of the berries and appears to be characteristic of the *Vacciniaceæ* for cranberries, *Vaccinium vitis Idæa* also yield the same reaction (Plahl, Zeitsch. Nahr. Genussm. 1907, 13, 1).

The sugar in bilberries is entirely invert sugar (Windisch and Boehm, Zeitsch Nahr. Genussm. 1908, 8, 347). The ash contains:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2
57·1	5·2	8·0	6·1	1·1	2·1	17·4	3·1	0·9

(Borggreve and Homberger, Bied. Zentr. 1886, 487).

Bilberries contain a red-brown dye, insoluble in acidified water and a soluble dye which, when boiled with acid, yields sugar and the insoluble colouring matter (Weigert, Bied. Zentr. 1896, 25, 58).

The juice of this berry (Ger. *Heidelbeere*) is used for colouring wines. The colouring matters of grapes and of bilberries behave in an almost identical way with most reagents (Andrée, Arch. Pharm. [3] 13, 90; Ber. 13, 582; Plahl, Chem. Zentr. 1907, i. 837).

To detect bilberry juice in wine, 50 c.c. of the wine is made faintly alkaline with sodium hydroxide, and evaporated to half its volume. After cooling it is made up to the original volume and precipitated with lead acetate. The filtrate is then precipitated with sodium sulphate and after filtration the solution is acidified with hydrochloric acid. If any vegetable colouring matter is still present, the solution at once becomes red, but the blue colour given by bilberry only appears on heating the solution in a boiling water-bath. In this way 2 p.c. of bilberry juice can be detected (Plahl, Chem. Zentr. 1908, i. 1482).

According to Vogel (Ber. 21, 1746), the colouring matter of grapes and of bilberries can be readily distinguished by their absorption spectra, providing the wine is not too concentrated, and after adding a trace of alum solution, it is carefully neutralised with ammonia. After long keeping, however, the colouring matters cannot be distinguished in this way.

The colouring matter of the juice can be extracted by neutralising it with caustic soda and then treating it with hide powder. After two days the hide powder containing the colouring matter is filtered off, washed with water, and treated with dilute hydrochloric acid, after which it is precipitated with dilute soda. The colouring substance, probably $C_{10}H_{12}O_3$, is soluble in mineral and organic acids, but insoluble in water, alcohol, ether, chloroform, or benzene. It reduces Fehling's solution, and is decomposed by hot conc. sulphuric acid, a compound $C_{14}H_{14}O_7$ being thrown down when water is added to the red solution thus obtained. The colouring matter is oxidised by nitric acid to oxalic and picric acids. It slowly decomposes on standing, evolving carbon dioxide, and its solution when treated with copper sulphate or zinc chloride, turns violet; with lead acetate it turns blue, and with ferric chloride dark-brown (Nachen, Chem. Zentr. 1895, 66, 1084).

Considerable quantities of citric and malic acids are present in the juice, which also contains hydrocarbons, glucoses, pentoses, and inosotol (Nachen, *l.c.*). Ammonia turns bilberry juice a brownish-green; nitric acid in the cold blue, changing to red and becoming orange on boiling; lead acetate gives a blue precipitate, copper sulphate a violet colour, sodium carbonate a blue-black, and borax an amaranth red (Griessmayer, Chem. Zentr. 8, 381).

When chlorine is passed into the juice, a bright-grey amorphous precipitate is obtained (Nachen, *l.c.*).

(For quantitative analysis of the juice, compare Mathes, Muller, and Ramstedt (Chem. Zentr. 1905, i. 407); Lühring, Bohrisch, and Hepner (*ibid.* 1907, ii. 1755); Shamm and Jegin (*ibid.* 1907, i. 983); Behre, Grosse, and Schmidt (*ibid.* 1909, i. 456).)

When the juice is fermented, the products include aldehyde, and capric, propionic, valeric, and butyric acids (Nachen, *l.c.*).

Wine has been prepared from bilberry juice by allowing it to ferment spontaneously when mixed with a third its weight of honey. The wine thus prepared bears prolonged storage, is rich in alcohol and tannin, is of a rich clear colour, and has an agreeable flavour (Graftien, Bl. Assoc. Belge des chim. 12, [3] 107; Otto, Bied. Zentr. 1899, 28, 284).

When bilberries are extracted with chloroform, the solution evaporated, and the residue extracted with light petroleum, the soluble portion yields a wax, m.p. 71°, and a crystalline compound, probably *vitin*, m.p. 255°–260° $[\alpha]_D + 60{\cdot}72°$ (Seifert, Landw. Versuchs-Stat. 45, 29).

BILE. Bile is the secretion of the liver which is poured into the duodenum (the first part of the small intestine). It can be collected in animals by means of a biliary fistula; the same operation has occasionally been performed in human beings. After death, the gall bladder yields a good supply of bile, which is more concentrated than that obtained from a fistula. The amount of bile secreted is differently estimated by different observers; in man it probably varies from 500 to 1000 c.c. per diem.

Its constituents are the bile salts proper (sodium glycocholate and taurocholate), the bile pigments (bilirubin and biliverdin), a mucinoid substance, small quantities of fats, soap,

cholesterol, lecithin, urea, and mineral salts, of which sodium chloride and the phosphates of calcium and iron are the most important.

Bile is a yellowish, reddish-brown, or green fluid, according to the relative preponderance of its two chief pigments. It has a musk-like odour, a bitter-sweet taste, and is alkaline to litmus. The specific gravity of human bile is 1·026 to 1·032 from the gall bladder, and about 1·011 when derived from a fistula. The greater concentration of gall-bladder bile is partly explained by the addition to it from the wall of that cavity of the mucinoid material it secretes. The following table will, however, show that the low percentage of solids in fistula bile is due mainly to paucity of bile salts. This is accounted for in the way first suggested by Schiff—that there is normally a bile circulation going on in the body, a large quantity of the bile salts that pass into the intestine being first split up, then re-absorbed and again synthesised and secreted. This would obviously be impossible in cases where all the bile is discharged to the exterior through a fistula. The following is the table in question, the results being the mean of several analyses of human bile:—

Constituents	Fistula bile	Gall-bladder bile
Bile salts	0·42	9·14
Cholesterol, lecithin, fat	0·07	1·18
Mucinoid material	0·17	2·98
Pigment	0·07	
Ash	0·66	0·78
Total solids	1·39	14·08
Water (by difference)	98·61	85·92

The *Fel bovinum purificatum* of the pharmacopœia is made by mixing ox bile with twice its volume of rectified spirit: this is set aside for 12 hours until the sediment subsides; the clear solution is decanted and evaporated on the water-bath until it acquires a consistence suitable for forming pills. The material so obtained consists mainly of bile salts, cholesterol, fats, salts, and a certain amount of the mucinoid material. Its yellowish-green colour is due to bile pigment. It is given in doses of 5 to 10 grains, usually as pills coated with keratin to obviate its deleterious action on gastric digestion. It is given mainly in cases where the natural secretion is absent or scanty, as in jaundice. But for a full description of its medicinal uses, and also for a description of the action of drugs (cholagogues) which stimulate the liver either to secrete more bile or to cause a discharge of bile already formed, the reader is referred to any standard text-book on Pharmacology.

Plattner's crystallised bile. The bile salts are soluble in water and in alcohol, but not in ether. Their solution in alcohol is therefore precipitated by ether, and this precipitate gives, with proper precautions in technique, rosettes or balls of fine needles, or 4–6 sided prisms composed of the bile salts. This preparation is known as Plattner's crystallised bile; it is usually made from ox bile, in which case the main constituent is sodium glycocholate.

The bile salts. The sodium salts of glycocholic and taurocholic acids are those most frequently found. The former is more abundant in the bile of man and herbivora, the latter in carnivora. Glycocholic acid ($C_{26}H_{43}NO_6$) is by the action of dilute alkalis and acids, and also in the intestine, hydrolysed and split into glycine (amino-acetic acid), and cholalic (cholic) acid

$$C_{26}H_{43}NO_6+H_2O=C_2H_5NO_2+C_{24}H_{40}O_5.$$

Its sodium salt has the formula $C_{26}H_{42}NaNO_6$. Taurocholic acid ($C_{26}H_{45}NO_7S$) similarly splits into taurine (aminoisethionic acid) and cholalic acid

$$C_{26}H_{45}NO_7S+H_2O=C_2H_7NO_3S+C_{24}H_{40}O_5.$$

Its sodium salt has the formula $C_{26}H_{44}NaNO_7S$. These substances usually are detected by Pettenkofer's reaction; small quantities of cane sugar and sulphuric acid added to the bile produce a brilliant purple colour. This is due to the interaction of furfuraldehyde (produced from the sugar and sulphuric acid) and cholalic acid.

Throughout the animal kingdom considerable variations are found in the bile salts. Thus in many fishes potassium instead of sodium salts are present. There are also variations in the bile acids themselves; for instance, in the pig hyoglycocholic acid ($C_{27}H_{43}NO_5$) takes the place of ordinary glycocholic acid, and in the goose chenotaurocholic acid ($C_{29}H_{49}NSO_6$) of ordinary taurocholic acid.

A good deal of work has been expended on the constitution of cholalic acid, but much yet remains to be done. According to Mylius, it is a monobasic alcohol acid with a secondary and two primary alcohol groups. Its formula may therefore be written $C_{20}H_{31}\begin{cases}CHOH\\(CH_2OH)_2.\\COOH.\end{cases}$ On oxidation it yields other acids, which have been named dehydrocholalic acid ($C_{24}H_{34}O_5$), bilianic acid ($C_{24}H_{34}O_8$), cilianic acid ($C_{20}H_{28}O_8$); on reduction desoxycholalic acid ($C_{24}H_{40}O_4$) is obtained.

Choleic acid is another cholalic acid, with the formula $C_{24}H_{40}O_4$, found in small quantities in the bile of ox and man. It is probably identical with desoxycholalic acid. Fellic acid ($C_{23}H_{40}O_4$) is still another acid obtainable from human bile along with the ordinary acid. The principal cholalic acid in bear's bile is termed ursocholeic acid ($C_{18}H_{28}O_4$ or $C_{19}H_{30}O_4$) by Hammarsten. The same investigator finds in the walrus that the principal bile acids are *α*-phocætaurocholic acid, the cholalic acid from which has the formula $C_{22}H_{30}O_5$; and *β*-phocætaurocholic acid, the cholalic acid from which differs in certain particulars from ordinary cholalic acid, although it has the same empirical formula; he terms it *iso*cholalic acid.

The bile pigments. Bilirubin has the formula $C_{16}H_{18}N_2O_3$, and biliverdin contains an atom more of oxygen ($C_{16}H_{18}N_2O_4$); in bile exposed to the air, bilirubin is fairly rapidly oxidised to biliverdin. It has been proved by physiological experiment that the bile pigment is an iron-free derivative of the blood pigment; it is, in fact, identical with the substance termed hæmatoidin, which occurs usually in crystalline form in extravasations of blood in the body, as in a bruise. The bile pigment shows no absorption bands with the spectroscope, and is detected by various colour reactions, of which the most familiar is Gmelin's test; this consists in the play of colours—green, blue, red, and finally yellow—produced by the oxidising

action of fuming nitric acid. The end or yellow product is called choletelin ($C_{16}H_{18}N_2O_6$). By reduction outside the body, a product called hydrobilirubin ($C_{32}H_{40}N_4O_7$) is obtained. A similar but not identical reduction product containing less nitrogen than hydrobilirubin is formed in the intestine, and constitutes stercobilin, the pigment of the faces. Some of this is absorbed and ultimately leaves the body in the urine, where it is termed urobilin. A small quantity of urobilin is sometimes found preformed in the bile.

Bile mucin. The viscous material in the bile of some animals (*e.g.* man) is true mucin; in other (*e.g.* the ox) it is a nucleoprotein.

Cholesterol. Of the other constituents of the bile, cholesterol or cholesterin is the most interesting; although normally present in traces only, it may occur in excess and form the concretions known as gall stones, which are usually more or less tinged with bile pigment. It is a monatomic unsaturated alcohol, with the empirical formula $C_{27}H_{45}\cdot OH$. Windaus and others have shown that it is a member of the terpene series, which had hitherto only been found as excretory products of plant life.

The physiological uses of bile.—Bile is doubtless to some extent an excretion. Some state that it has a slight lipolytic action; and in some animals it certainly has a feeble diastatic power. Its main action, however, is to assist pancreatic digestion; this it does not only because its alkalinity is useful in helping to neutralise the acid mixture which leaves the stomach (chyme), but it also acts as a coadjutor to the enzymes of pancreatic juice. This is true for the proteolytic enzyme (trypsin), and the amylolytic enzyme (amylopsin), but is especially so in the case of pancreatic lipase; some go so far as to speak of the bile salts as the co-enzyme of this ferment.

In virtue of the properties which the bile salts possess of lowering surface tension, the products of fat-cleavage pass more rapidly through membranes moistened with bile than through these which are not. There is a good deal of evidence that the same holds *intra vitam*, and thus the presence of bile aids the absorption of fats by the mucous membrane which lines the intestinal wall. Bile also is a solvent of fatty acids.

When the bile meets the chyme, the turbidity of the latter is increased owing to the precipitation of unpeptonised protein. This action of the bile salts is probably useful, as it converts the chyme into a more viscid mass, and somewhat hinders its progress along the first part of the intestine, so allowing digestion and absorption to occur there.

Bile is said to be a natural antiseptic, but it is very doubtful if it is really efficient in reducing the putrefactive processes in the bowel. The bile salts are *in vitro* very feeble germicides, and the bile itself is readily putrescible; any power it may have in lessening putrescence in the intestine is due chiefly to the fact that by increasing absorption it lessens the amount of putrescible material in the intestinal tract. It is stated also that bile increases the peristaltic action of the large intestine.

Industrial and commercial uses of bile.—Apart from a somewhat limited use as a therapeutic agent, to which allusion has already been made, bile has but little commercial importance. It is, however, employed for cleansing woollen goods, and, as housekeepers know, is specially useful in cleaning carpets. This is probably connected with its power of lowering surface tension. Bile is also used by artists to ensure the uniform spreading of water colours on paper.

No attempt has been made in the foregoing article to allude to the very extensive literature of bile. This relates almost exclusively to the physiology and pathology of bile, and the important references can be best obtained from some standard work on Physiological Chemistry, such as Hammarsten's. W. D. H.

BIRCH BARK. *Betula.* (*Birke*, Ger.; *Bouleau*, Fr.) The inner bark is used in India as a substitute for paper and for lining the roofs of houses (Dymock, Pharm. J. [3] 10, 661).

It contains good tanning materials, yielding bright-yellow leather (Wagner's Jahr. 30, 1206; Trotman and Hackford, J. Soc. Chem. Ind. 1905, 1096; Bögh, Chem. Zentr. 1906, i. 1915).

The dry distillation of birch bark yields a tar and an acid aqueous solution (Kuriloff, J. Russ. Phys. Chem. Soc. 23, 98). The chief constituents of birchwood tar creosote are guaiacol and 1 : 3 : 4-creosol, together with traces of phenol, cresol, and 1 : 3 : 4-xylenol (Pfreager, Arch. Pharm. 228, 713). According to Hirschsohn (Pharm. Centr. H, 1903, 44, 845) birch tar is often adulterated with crude naphtha or naphtha residues, but the adulterated can be distinguished from the pure product by the fact that the former is only partially soluble in acetone, whereas the latter is wholly soluble.

When warm birch tar is treated with air, oxygen, or ozonised air, a pleasant-smelling solid product is obtained, soluble in alkalis, but almost insoluble in alcohol, benzene, and ether. It and its salts can be employed in medicine, pharmacy, and technically. At the same time, readily condensible liquid products distil over, which can also be used medicinally and technically, as antiseptics and in perfumery (Friedländer's Fortschr. der Teerfabr. 1905–7, 930).

A colouring substance employed in pharmaceutical and cosmetic preparations is obtained when the bark of young birch trees is soaked in water containing about $\frac{1}{20}$ of its weight of bicarbonate of soda or other carbonate. It is then boiled and filtered. Hydrochloric acid is added to the red-brown filtrate until a precipitate is formed which is filtered, washed, and dried at a gentle heat. It should be kept in well-stoppered vessels (Friedländer's Fortschr. der Teerfabr. 1897–00, 661).

The bark contains a crystalline substance termed *betulin* $C_{33}H_{60}O_3$, m.p. 257·8°, sublimes in a current of air, readily yields an anhydride at 130°, and is tasteless and odourless. It does not combine with acids or alkalis, is insoluble in water, sparingly soluble in alcohol, readily in ether and turpentine.

It is prepared by mixing the powdered epidermis of *Betula alba* with 1–8 p.c. of potassium nitrate, pressing the mixture into small tablets, and burning them in closed chambers without flame, and with the introduction of a regulated supply of air. The betulin so formed is used as films for certain substances in which it acts as an antiseptic, as a protection against

damp or against corrosive acids (Wheeler, Pharm. J. 1899, 494).

The films can be deposited direct on various substances by allowing the vapours to play upon them. By a slight modification the films can be made to have a greater or less degree of transparency and porosity (Wheeler, Chem. Zentr. 1900, ii. 798).

According to Wheeler (J. Soc. Chem. Ind. 1899, 606), when birch bark or materials made from the latter, containing betulin are heated in a closed chamber and in a current of air, substances termed *pyrobetulin* and *pyrobetulin anhydride* are produced in forms other than films.

Gaultherine $C_{14}H_{18}O_8,H_2O$, a glucoside, is obtained by extracting the bark of *Betula lenta* with alcoholic lead acetate, precipitating by ether, and recrystallising from alcohol. The aqueous solution has a bitter flavour, is lævo-rotatory, and reduces Fehling's solution when boiled. It is hydrolysed by mineral acids, baryta, and by water when heated to 130°–140°, giving a sugar and methyl salicylate (Schaugans and Geroch, Arch. Pharm. 232, 437).

A gum of probable formula $C_4H_6O_3$ has been isolated from American birch wood (*Betula alba*) (Johnson, Amer. Chem. J. 1896, 214).

Birchbark oil is obtained by distilling birch bark (*Betula alba*) in steam. It is brown, and has a similar odour to birch bud oil. On cooling, crystals separate. It contains palmitic acid (Haensel, Chem. Zentr. 1907, ii. 1620; Ziegelmann, Pharm. Review, 1905, 23, 83).

The birch bark oil prepared from the bark of *Betula alba* by Haensel (Chem. Zentr. 1908, ii. 1436), had sp.gr. 0·9003 at 20° and $[\alpha]_D$ −12·08°; a colourless monocyclic sesquiterpene was isolated from it, having b.p. 255°–256°/744 mm., sp.gr. 0·8844 at 20°, and $[\alpha]_D$ −0·5°. The terpene yields a hydrochloride, sp.gr. 0·9753 at 20°, and a hydrocarbon, b.p. 258°–260°/747 mm., and sp.gr. 0·8898 at 20°.

Birch oil, or the wintergreen oil of commerce, is obtained from the twigs of North American birches, especially the *Betula lenta*, but the pure genuine oil is prepared from *Gaultheria procumbens* (J. Soc. Chem. Ind. Abstr. 1893, 174). It consists of methylsalicylate, a hydrocarbon $C_{15}H_{24}$, and small quantities of benzoic acid and ethyl alcohol (Schroeter, Amer. J. Pharm. Aug. 1889; Trimble and Schroeter, Pharm. J. 20, 166; Ziegelmann, *l.c.*).

Oil of *Gaultheria procumbens* contains 99 p.c. methylsalicylate, together with some paraffin —$C_{30}H_{62}$—probably triacontane; an aldehyde or ketone; a secondary alcohol $C_8H_{16}O$, and an ester $C_{14}H_{24}O_2$, and is lævo-rotatory, sp.gr. 1·180; that obtained from the birch contains 99·8 p.c. methylsalicylate, together with the above constituents except the alcohol $C_8H_{16}O$, which is absent. It is optically inactive; sp.gr. 1·187 (Pharm. J. 1895, 307, 328).

Birch bud oil is obtained by the distillation of birch buds with steam. It is yellow, and has a pleasant aromatic odour. Crystals separate out at ordinary temperatures, and it becomes wholly crystalline at −45° (J. Soc. Chem. Ind. 1903, 228). It is soluble in alcohol and in ether, but not in alkalis, carbon disulphide, or glacial acetic acid. It is lævo-rotatory, its rotation and specific gravity varying with different preparations. That obtained by Schimmel (Chem. Zentr. 1909, ii. 2156) had sp.gr. 0·9730 at 15° and α_D −5° 34′.

It contains a paraffin, m.p. 50°, an ester, and a sesquiterpene alcohol, *betulol*, probably $C_{15}H_{23}OH$, which is very much like amyrol (obtained from sandalwood oil), has a bitter taste, an odour like incense, b.p. 284°–288°/743 mm., 138°–140°/4 mm.; sp.gr. 0·975; $[\alpha]_D$ −35° (von Soden and Elze, Ber. 38, 1636; Haensel, Chem. Zentr. 1909, ii. 1156. Compare also Pharm. Zeit. 47, 818; Schimmel, Chem. Zentr. 1905, i. 1340).

The leaves of *Betula alba* yield an olive-green oil, which is solid at ordinary temperature, but fluid at 35°, has sp.gr. 0·9074 at 35°, and is optically inactive (Haensel, Chem. Zentr. 1904, ii. 1737).

Haensel (Chem. Zentr. 1908, i. 1837) has isolated a crystalline paraffin, m.p. 49·5°–50°, from the oil of birch leaves.

According to Grasser and Purkert (Chem. Zentr. 1910, i. 489), products $C_{41}H_{70}O_7$, $C_{39}H_{68}O_3$, readily soluble in water, and of which the potassium salt $C_{41}H_{67}K_3O_7$ can be used therapeutically as a diuretic, can be obtained by extracting birch leaves with alcohol, treating the warm extract with potassium hydroxide, and then saturating the solution with dry carbon dioxide. Water is now added and the insoluble products filtered off. The filtrate is concentrated, the soluble products precipitated with a mineral acid, and separated from one another by conversion into their di- and tri-alkali derivatives.

Birch juice obtained from birch trees contains lævulose, a large quantity of malates, and basic constituents. When fermented with dextrose and milk of almonds, it forms 'birch wine' (Lenz, Ber. Deut. Pharm. Ges. 19, 332).

BIRD-LIME. (*Glu*, Fr.; *Vogelleim*, Ger.) Bird-lime, from *Ilex aquifolium* (Linn.), was found by Personne to consist, in addition to vegetable *débris* and water, of calcium oxalate, caoutchouc, and ethereal salts of a solid crystalline substance, *ilicic alcohol* $C_{25}H_{44}O$, m.p. 175°, with undetermined fatty acids.

According to Divers and Kawakita, Japanese bird-lime, made from *I. integra*, contains ethereal salts of palmitic acid, and in very small quantity a semi-solid acid, the calcium salt of which is soluble in ether and in alcohol. Japanese bird-lime also yields two very similar alcohols by hydrolysis, one differing only slightly from ilicic alcohol, and termed *ilicylic alcohol* $C_{22}H_{38}O$, m.p. 172°, and another named *mochylic alcohol* $C_{26}H_{46}O$, m.p. 234°, from *mochi*, the Japanese word for bird-lime.

Caoutchouc is also present in Japanese bird-lime to the extent of about 6 p.c., but only minute quantities of oxalates. By distillation, bird-lime yields much palmitic acid and a thick oily hydrocarbon $C_{26}H_{44}$ (Divers and Kawakita, Chem. Soc. Trans. 1888, 268).

BIREEZ. Persian name for gum galbanum (Dymock, Pharm. J. [3] 9, 1016).

BISDIAZONIUM SALTS *v.* DIAZO COMPOUNDS.

BISMAL. Bismuth methylene digallate (*v.* BISMUTH, Organic compounds of; also SYNTHETIC DRUGS).

BISMARCK BROWN *v.* AZO- COLOURING MATTERS.

BISMITE. Native bismuth oxide, Bi_2O_3, occurring as a yellow earthy powder, or as minute rhombohedral scales. L. J. S.

BISMON *v.* SYNTHETIC DRUGS.

BISMUTH. *Bismuth.* (*Etain de glace*, Fr.; *Wismuth*, Ger.) Symbol Bi. At. wt. 208·0.

Occurrence.—Metallic bismuth occurs in small quantities in widely distributed localities, usually with other ores, such as those of cobalt, nickel, copper, silver, lead, and tin. It is found massive, granulated, reticulated or arborescent, associated with arsenic and silver, and occasionally iron.

The principal districts are Adelaide in South Australia, Altenberg, Schneeberg, Annaberg, Marienberg, Joachimsthal, Johanngeorgenstadt, Lölling in Carinthia, Fahlun, Sweden, and New South Wales. In small quantities it occurs at Huel Sparnon, Cornwall, Carrick Fells, Alva, Stirlingshire, and in Bolivia. Alloyed with 64 p.c. gold it occurs at Maldon, Victoria. Alloyed with tellurium it occurs as *tetradymite* in Cumberland. An alloy of bismuth with 3 p.c. arsenic occurs at Palmbaum near Marienberg.

Bismuth sulphide is widely distributed in small quantities, being found in Saxony, Sweden, South Australia, America, and Cumberland. A sulphide of bismuth, copper, and lead occurs as *needle ore*, *aciculite*, or *patrinite*.

As oxide, or *bismuth ochre*, it is found as a yellow substance, frequently as a coating on other minerals, associated with iron and other impurities, at Schneeberg, Joachimsthal, Beresof in Siberia, and in New South Wales. The principal ore in Bolivia, which is stated by Domeyko to be the richest country in bismuth, is a compact earthy hydrated oxide.

Bismuth occurs as carbonate or *bismuthite*, usually containing carbonates of iron and copper, at Meymac, with antimony, arsenic, lead, iron, and lime; in Mexico, whence it is imported to this country; in North Carolina, and other localities. Of late years considerable deposits of bismuth ores have been found in many places in America, but they have been very little worked. The supply of bismuth ore would much exceed the demand were it not for an agreement between the smelters and the mining companies by which the supply is restricted and the price of the metal maintained at a remunerative figure.

Bismuth is stated to occur in most sulphurous copper ores in about the same proportions as silver in galena, in other copper ores except the carbonate, and in most samples of commercial copper and copper coins (Field and Abel, Chem. Soc. Trans. 16, 304; and Field, Chem. News, 36, 261).

Extraction.—At Schneeberg in Saxony the ore worked is principally metallic bismuth occurring in ores which contain silver, lead, tin, and arsenic in gneiss and clay-slate.

The ore, which contains from 7 to 12 p.c. bismuth, is sorted by hand as far as possible from the gangue before treatment. The old method of *liquation* or 'sweating' is still used, but has now been largely superseded by smelting processes, in which the metal is much more perfectly extracted.

Liquation.—In this process the metal is separated as far as possible from the gangue by melting at a low temperature. The picked ore is broken into pieces as large as a hazel nut, and placed in inclined iron tubes in charges of about 12 cwts., sufficient space being left in the tube for stirring the ore from the upper end (Figs. 1, 2, 3). The tubes are closed at the upper ends by plates of iron, and at the lower ends by similar plates containing circular apertures through which the molten metal may run. The ends of the tubes project slightly beyond the walls of the furnace, the upper over a tank and the lower ends over iron crucibles which contain powdered charcoal, and which are gently heated from below by a small charcoal furnace. The tubes are heated so as to cause the metal to flow easily, and in about 10 minutes the bismuth commences to pass out into the crucibles, being there covered by the charcoal and thus protected from oxidation. The ore is occasionally stirred with an iron rod from the upper end, and in from 30 to 60 minutes the operation is completed. The residues, *graupen* or *bismuth barley*, are raked from the upper end into the tank, and at once replaced by fresh ore. In this manner only about two-thirds of the bismuth is extracted. 20 cwts. of ore require 63 cubic feet of wood. The contents of the pots are removed by ladles to moulds and cast into ingots of 25 to 50 lbs. weight.

Sulphurous ores are usually roasted to remove sulphur, and then smelted with iron (to remove the last traces of sulphur), carbon, slag, sodium carbonate, limestone, and sometimes fluor-spar. The regulus of bismuth thus obtained is fused on an inclined iron plate and run down, leaving a dross containing much of the impurity. Bismuth ores are sent from Joachimsthal, and worked by this process at Schneeberg.

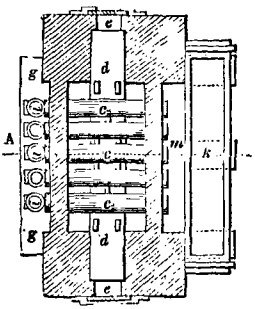


FIG. 1.

The following analyses of two typical samples show the composition of commercial bismuth: From Saxony—Bismuth, 99·77 p.c.; copper, 0·08; silver, 0·05; sulphur, 0·10; iron, trace. From Joachimsthal—Bismuth, 99·32 p.c.; lead, 0·30; silver, 0·38; iron and copper, traces; sulphur, none. About 10,000 lbs. of bismuth are annually produced at Schneeberg.

At Joachimsthal a method devised by R.

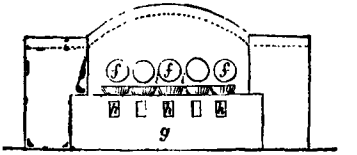


FIG. 2.

Vogel is used (Dingl. poly. J. 167, 187) for extracting bismuth from ores free from lead. The ores, which usually contain from 10 to 30 p.c. bismuth, are mixed, according to their richness, with 23 to 30 p.c. iron turnings, 15 to 50 p.c.

sodium carbonate (according to the amount of gangue present), 5 p.c. lime, and 5 p.c. fluor-spar. The mixture is introduced in charges of about 1 cwt. into clay crucibles, 23 inches high and 16 inches wide at the mouth, covered and heated in a wind furnace to tranquil fusion, and poured into conical moulds. The liquid separates into three layers, the upper consisting of slag, the second of a speiss containing the arsenic, sulphur, nickel, cobalt, and iron, and most of the other impurities, with about 2 p.c. of bismuth, and the lower consisting of a regulus of nearly pure bismuth. The metal is again fused and remoulded (*see* Kerl, Handb. der Met. Hüttenkunde).

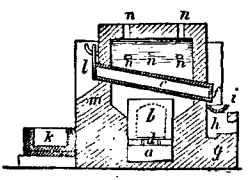


FIG. 3.

A similar process has been adopted by Patera (J. 1862, 646) for the extraction of bismuth from refinery residues.

In France the carbonate of bismuth imported from Meymac is dissolved in the minimum quantity of hydrochloric acid and pieces of iron inserted in the slightly acid liquid. The bismuth is thus precipitated as a black powder, which is well washed and fused in a plumbago crucible under a layer of charcoal at as low a temperature as possible (Ad. Carnot, Ann. Chem. Phys. [5] 1, 405; and Bull. Soc. chim. 21, 114).

For the extraction of bismuth for pharmaceutical purposes from sulphurous ores, Valenciennes roasts the ore on the level bed of a reverberatory furnace for 24 hours with the occasional addition of charcoal and frequent stirring with an iron rabble. When the sulphur has thus been evolved, the ore is mixed with about 30 p.c. charcoal, and a mixture of chalk, salt, and fluor-spar, and again fused in a reverberatory furnace. From 5 to 8 p.c. of the bismuth is lost by this process, but this is compensated by the extra purity of the product. By subsequent fusion with nitre, the antimony, arsenic, and sulphur are removed, and by the ordinary wet methods the lead, copper, and silver are eliminated (M. A. Valenciennes, Ann. Chim. Phys. [5] 1, 397). Ores of bismuth averaging 60 p.c. bismuth are imported into England to the extent of about 40 tons annually, principally from Adelaide, South Australia, and from Mexico. They are usually fused in black-lead pots with borax, sodium carbonate, and a little crude tartar.

H. Tamm (Chem. News, 25, 85) states that bismuth can be separated from ores containing much copper by fusion with an alkaline flux containing free sulphur, in which case the copper remains unreduced. He recommends a mixture of 5 parts sodium carbonate, 2 salt, 1 sulphur, 1 carbon, to be mixed in about equal proportions with the ore. The bismuth produced is stated to be much more free than usual from arsenic, antimony, and lead, but about 8 p.c. of the total bismuth is lost. The bismuth present in small quantities in lead, copper, and silver ores frequently becomes concentrated in the secondary products of the metallurgical processes and may then be profitably extracted. In the oxidation of silver-lead containing bismuth, the lead oxidises much more rapidly than the bismuth, and at the close of the cupellation a blackish litharge rich in bismuth is obtained, from which that metal may be extracted by reduction and cupellation (J. 12, 711). In this manner bismuth becomes concentrated in the *blicksilber* in the refinement of silver ores at Freiberg, and passes into the hearth bottoms, as much as 25 p.c. being sometimes so absorbed. When the hearths contain sufficient bismuth to be profitably extracted, they are finely ground and treated with hydrochloric acid, with the formation of bismuth chloride. Water is added to the solution to precipitate the metal as oxychloride, and the precipitate is collected, washed, dried, and reduced to metal by fusion with charcoal, sodium carbonate, and powdered glass (*v.* Phillips's Metallurgy).

Several proposals have been made for the extraction of bismuth by wet methods. Becker (Fr. Pat. 366439, 1906) suggests the treatment of sulphide ores with a solution of an alkali or alkaline earth hyposulphite. The solution thus obtained is treated with alkali sulphides, and the resulting precipitate of bismuth sulphide is dried and smelted as described above.

Both Becker (*ibid.*) and Ranald (Eng. Pat. 16622, 1898) have patented the use of a solution of ferric chloride as a solvent for bismuth sulphide and the subsequent precipitation of metallic bismuth from the solution by means of iron or zinc, or by electrolysis.

Eulert (Rev. Prod. Chim. 4, 164) employs a mixture of sulphuric acid, water, common salt, and potassium nitrate as the extracting liquor, and the process can be made continuous. The bismuth is finally obtained as the oxychloride, which can be sold or smelted for the metal.

On the extraction of bismuth from its ores, *v.* also Winckler (Ber. Entwick. Chem. Ind. 1, 953).

Purification.—The crude bismuth produced by the above methods contains a variety of impurities, from which it is important in many cases to separate it. These impurities are sulphur, arsenic, antimony, copper, nickel, cobalt, silver, lead, and a trace of iron.

Sulphur and arsenic may be removed by fusion with $\frac{1}{10}$ of its weight of potassium nitrate, with constant stirring at a temperature slightly above the temperature of fusion; the nitre soon oxidises the impurities and a little of the bismuth, forming with them a slag which rises and solidifies at the surface. For the complete removal of these impurities a second fusion is frequently necessary.

C. Méhu (Pharm. J. [3] 4, 341) recommends the following process for the removal of sulphur and arsenic. The metal is heated considerably above the melting-point in a vessel so as to expose a large surface, and the oxide is removed to the sides as fast as it forms until about one-fourth of the metal has become oxidised; the greater part of the sulphur and arsenic will then have passed off as oxides. The mass is cooled, pulverised, and mixed with charcoal, dried soap, and potassium carbonate (free from sulphate), about one-fourth of the original weight of the metal, in a crucible, covered with charcoal, and heated to redness for one hour. It is thence removed and again fused in contact with air to remove the potassium which it contains, and which separates as a white film on the surface. Arsenic

may also be mostly removed by fusion for a considerable time under a layer of charcoal. Arsenic, sulphur, and most of the antimony may be eliminated by fusion at a bright-red heat under borax, stirring with a rod of iron until the action ceases. The iron combines with the impurities and rises as a difficultly fusible slag to the surface from beneath which the still liquid metal may be poured after partial cooling.

For the complete removal of *antimony*, 2 or 3 parts of bismuth oxide for each part of antimony supposed present are fused with the metal. The oxide of bismuth then gives up its oxygen to the antimony, becoming itself reduced and the antimonious oxide floats on the surface.

Hugo Tamm (Chem. News, 25, 85) recommends for the removal of *copper* the fusion of the metal at a low temperature under 1 part of a mixture of 8 potassium cyanide and 3 sulphur. When the action has ceased the mass is stirred with a clay (not iron) rod, cooled until the flux has set, and the metal poured out from beneath. If impure cyanide is used, a relatively larger quantity is required.

Iron may be completely removed, according to H. Türach (J. pr. Chem. [2] 14, 309), by fusion under a layer of potassium chlorate containing from 2 to 5 p.c. sodium carbonate.

From *silver* bismuth may be separated by cupellation and subsequent reduction of the bismuth oxide so produced, or the metal may be dissolved in nitric acid, the silver precipitated with hydrochloric acid, the solution filtered, and the basic salt of bismuth precipitated by excess of water, and reduced to metal.

Silver can be partially removed from bismuth by a process resembling Pattinson's process for lead (Schneider, J. pr. Chem. [2] 23, 75).

Lead may be precipitated from a nitric acid solution of the metal by the addition of sulphuric acid, and the bismuth recovered as already described. A method commonly used is to fuse the impure metal with bismuth oxychloride, from which the lead liberates bismuth, itself becoming combined with oxygen and chlorine.

A number of investigations on the refining of bismuth have been conducted by E. Matthey, and the methods he proposes are given separately below, inasmuch as they possess the merit of simplicity and have been thoroughly tested on a large scale.

Arsenic is removed completely by maintaining molten bismuth at a temperature of 510°–520° for some time. There is only a very slight loss due to oxidation (E. Matthey, Chem. News, 67, 63).

Antimony is separated by melting the metal and maintaining the temperature at 350°. An alloy of bismuth and antimony, containing over 30 p.c. of the latter, rises to the surface of the metal, giving it an 'oily' appearance, and can be skimmed off. A complete removal of the antimony is thus effected (E. Matthey, *l.c.*).

Copper. For the separation of copper from bismuth which has been previously freed from arsenic, antimony, lead, &c., E. Matthey (Roy. Soc. Proc. 43, 172) recommends its fusion with bismuth sulphide. The pure metal obtained amounts to 90 p.c. of the crude material, while the remaining bismuth sulphide, containing copper sulphide, may be resmelted.

Alkali sulphides may be substituted for the bismuth sulphide in the above operation (E. Matthey, Proc. Roy. Soc. 49, 78).

Lead may be separated from the fused metal by repeated crystallisations, the alloy of bismuth and lead melting at lower temperatures than the purer bismuth. E. Matthey has thus by four crystallisations reduced the percentage of lead from 12 to 0·4 p.c. (Proc. Roy. Soc. 42, 93).

For the separation of *gold* and *silver*, E. Matthey (Proc. Roy. Soc. 42, 89, 94) recommends the addition of 2 p.c. zinc to the molten metal. The mass is gradually cooled and the surface crust removed. This operation is repeated, whereby the whole of the precious metals are concentrated in the skimmings. On fusing these in a crucible with borax, the gold and silver are freed from impurities by the action of the oxide of bismuth, and sink to the bottom. To separate the last traces of these metals from the slag, it is again fused with bismuth.

A. Mohr states (Elektrochem. u. Met. Ind. 1907, 5, 314) that an electrolytic method has been used with success for the purification of a Mexican lead-bismuth alloy containing 81·1 p.c. lead and 14·5 p.c. bismuth, together with small amounts of antimony, iron, zinc, arsenic, silver, and gold. First the metal is made the anode in an electrolyte containing 6 p.c. lead fluosilicate and 14 p.c. hydrofluosilicic acid. The lead is deposited on this cathode of pure lead, and contains only 0·01 p.c. bismuth. The anode slimes are fused with sodium hydroxide and carbonate, and the metal, containing 94 p.c. bismuth, cast into anodes, which are then used in a second electrolysis, using a solution of bismuth chloride (about 10 p.c.) and free hydrochloric acid (about 10 p.c.). The cathodes are of Acheson graphite, and are placed on the floor of the cell. The current used is 20 amp. per sq. ft. at the cathode, and 60 amp. per sq. ft. at the anode, with a P. D. at the terminals of 1·2 volts. The resulting bismuth is 99·8 p.c. pure, the remaining 0·2 p.c. consisting chiefly of silver. (*See* also Zahorski, Hurter and Brock, Eng. Pat. 22251, 1895.)

Chemically pure bismuth is best prepared by dissolving the commercial metal in nitric acid, decanting from any residue, and adding excess of water, whereby the bismuth is precipitated as basic nitrate, leaving the impurities in solution. The precipitate is well washed by decantation, dried, mixed with black flux or other reducing agent which produces a readily fusible flux, and reduced at a gentle heat in a crucible.

Properties.—Bismuth is a greyish-white crystalline metal of distinctly red tinge when compared with whiter metals such as zinc or antimony. It is very brittle and easily powdered, and a bad conductor of heat and electricity. Its tenacity is very small, a rod 2 mm. in diameter will just support a weight of 14·19 kilos. (Muschenbroeck). It forms fine obtuse rhombohedral crystals, which approach very closely to the form of cubes. It has also been obtained in the form of acicular needles, which are really elongated hexagonal prisms (Heberdey, Ber. Akad. Wien. 104, i. 254). Bismuth melts at 264° (Roscoe and Schorlemmer), and boils at a temperature between the melting-point of copper and nickel, *i.e.* between 1090° and 1450° (Carnelley and Carlton Williams), condensing in laminæ. The vapour density at

temperatures between 1600° and 1700° is 11, which corresponds to that calculated for a mixture of monatomic and diatomic molecules (Meyer, Ber. 1889, 22, 726). Its sp.gr. at 12° is 9·823. Scheerer and Marchand have stated that, on exposure to great pressure, the density of bismuth is *lowered*. W. Spring, however, has shown that the density is thereby *increased*. By exposure of bismuth of density 9·804 to a pressure of 20,000 atmospheres, the density was raised to 9·856; a second compression still further increased the density to 9·863 (Ber. 16, 2724). It is stated that by careful hammering its density may be raised to 9·88.

Bismuth expands in cooling. Tribe (Chem. Soc. Trans.) has shown that this expansion does not take place until after solidification.

Exposed to dry air, bismuth remains unaltered at the ordinary temperature, but in moist air or in contact with water it becomes coated with oxide. When heated in air it burns with a bluish flame, evolving yellowish fumes of oxide. At high temperatures it decomposes water.

Cold sulphuric acid has no action, but the hot concentrated acid dissolves bismuth. Hydrochloric acid acts but slowly, and Ditte and Metzner have shown (Compt. rend. 115, 1303) that this action can only take place in presence of oxygen. Nitric acid, dilute or strong, dissolves it readily, with the formation of nitrate. Powdered bismuth thrown into chlorine gas ignites with the formation of trichloride. It also unites directly with bromine, iodine, and sulphur.

When comparatively pure, bismuth crystallises readily. To obtain it in the form of fine crystals it is melted and allowed to cool until a crust has formed; the crust is pierced on opposite sides with a hot iron, and the still liquid portion poured through one of the openings. On careful removal of the crust the sides of the vessel are found covered with crystals, frequently resembling hollow pyramidal cubes like those of salt, but which are in reality obtuse rhombohedra. Their iridescent lustre is due to a very thin film of oxide which shows the colour characteristic of thin plates.

Bismuth can be obtained in the colloidal state by reducing a solution of the nitrate with stannous chloride, or by the action of hypophosphorus acid on bismuth oxychloride (Gutbier and Hofmeyer, Zeitsch. anorg. Chem. 44, 225).

Bismuth is the most diamagnetic substance known, a bar of the metal placing itself equatorially between the poles of a magnet, *i.e.* at right angles to the position taken up by a bar of iron. Bismuth also occupies an extreme place in the thermo-electric series, being used with antimony in the preparation of the most delicate thermopiles.

Analysis.—All compounds of bismuth, when mixed with carbon or other reducing agent and fused before the blowpipe, give a *brittle* white bead of metal and a yellow incrustation on the charcoal, darker than that of oxide of lead.

A very good dry test for bismuth is that due to von Kobell. The substance is heated on charcoal with a mixture of potassium iodide and sulphur, when, if bismuth is present, a brilliant scarlet incrustation is obtained.

Salts of bismuth in solution give, on addition of excess of water, a white precipitate of basic salt, which is insoluble in tartaric acid, and blackens with sulphuretted hydrogen (distinction from antimony).

Metallic iron, copper, lead, and tin precipitate metallic bismuth from solutions.

A qualitative test for bismuth proposed by Reichard (Chem. Zeit. 28, 1024) is the addition of a brucine salt, or, better, brucine itself to the solution. In presence of bismuth a deep-red colour is produced which is distinguished from that given by nitric acid by the fact that it becomes deeper on heating, whereas the colour given by nitric acid turns to yellow.

Estimation.—Bismuth may be separated from copper, cadmium, mercury, and silver, lead having been removed previously by precipitation as sulphate, by the following method, due to Stähler and Scharfenberg (Ber. 38, 3862).

The solution, which may contain hydrochloric acid, and should contain about 0·1–0·2 gram of bismuth, is diluted to 300–400 c.c., and any precipitate redissolved by the cautious addition of nitric acid. This solution is heated to boiling, and treated with a boiling 10 p.c. solution of trisodium phosphate Na_3PO_4 (obtained by mixing equivalent amounts of sodium hydrogen phosphate and caustic soda). In presence of much hydrochloric acid, a considerable excess of the phosphate must be used, but, should the solution become alkaline, nitric acid must be added. After boiling the whole for some time, the precipitate is allowed to settle, and the supernatant liquid is tested with sodium phosphate. If precipitation is complete, the precipitate is collected hot on a Gooch crucible, washed with 1 p.c. nitric acid, containing ammonium nitrate, dried at 120°, and finally heated over a bunsen burner, and weighed as bismuth phosphate $BiPO_4$. The precipitate is very hygroscopic: suitable precautions must therefore be taken in weighing it.

A modification of this method, which renders it suitable for the separation of bismuth from considerable amounts of mercury, has been described by Stähler (Chem. Zeit. 31, 615).

A volumetric method for the estimation of bismuth, for which considerable accuracy is claimed, is the chromate method of Löwe as modified by Rupp and Schaumann (J. Soc. Chem. Ind. 1902, 1558).

H. W. Rowell has published a method (J. Soc. Chem. Ind. 1908, 102) for the estimation of small quantities of bismuth in ores, &c. The method is colorimetric, depending on the yellow colour produced when potassium iodide is added to a solution of the bismuth compound in sulphuric acid (*see* also Eng. and Mining Jour. 1901, 459).

An account of other methods used for the estimation of bismuth will be found in the article on ANALYSIS.

For the dry assay of bismuth ores the fluxes used must depend on the composition of the ore. Thus with ores containing metallic bismuth or that metal as oxide, sulphide, carbonate, &c., a flux consisting of a mixture of 2 parts potassium or sodium carbonate, 1 part sodium chloride, and a proper quantity of argol or potassium cyanide or charcoal powder, will be useful (Tamm); with the addition, where much earthy matter is present, of borax. Where much *copper* is present, Tamm advises the use of one part of the ore mixed with one part or less of a mixture of

sodium carbonate 1, salt 2, sulphur 2, charcoal powder 1 part. The exact proportions in which these fluxes are most useful must be learned by experience.

Alloys of Bismuth.

Bismuth unites readily with most metals, forming alloys which are usually of great hardness, brittleness, and fusibility, and most of which expand on solidifying.

Lead containing very little bismuth, is toughened without becoming more brittle. The addition of bismuth to lead increases its hardness and tenacity; the alloy of 3 lead and 2 bismuth has ten times the hardness and twenty times the tenacity of lead. The alloy of 66 lead and 34 bismuth is very ductile, melting at 166°; it corresponds to $BiPb_2$. An alloy containing equal weights of the two metals is brittle, of foliated texture, and of the colour of bismuth. Its density is 10·709, *i.e.* greater than the mean density of the constituents.

Tin. The addition of bismuth to tin in small quantities renders it more elastic and sonorous. An alloy of 54 tin, 46 bismuth is crystalline and brittle; it melts at 133° (Guthrie, Phil. Trans. [5] 17, 464). The alloy of 24 tin, 1 bismuth is somewhat malleable, but a further addition of bismuth renders it brittle.

Tin and Lead. The alloys of bismuth with these two metals are of special interest. They are extremely fusible, and on account of their expansion on cooling they take a very fine impression, being largely used for electrotype moulds, &c.

An alloy of 1 bismuth, 2 tin, 1 lead is used as a soft solder by pewterers, and for the cake moulds for toilet soap. An expensive but effective alloy for stereotype clichés and metallic writing pencils contains 5 bismuth, 2 tin, 3 lead; it melts at 91·66°.

For special work *solder* containing bismuth is employed. It can be used under boiling water if a little hydrochloric acid is added.

A thorough physico-chemical investigation of these ternary alloys has been made by Charpy (Compt. rend. 126, 1569), whose memoir should be consulted for details. He finds that the eutectic mixture contains 32 p.c. lead, 16 p.c. tin, and 52 p.c. bismuth, and has m.p. 96°. Such alloys are used to a considerable extent in safety plugs for boilers and for automatic sprinklers.

The varieties of *fusible metal* contain these three metals, with the addition sometimes of cadmium, which still further lowers the melting-point. A table of the most important of these alloys is given below:

Name of alloy	Bismuth	Lead	Tin	Cadmium	Mercury	Melting-point	Temperature of maximum density
Newton's . .	50	31·25	18·75	—	—	94·5°	—
Rose's . . .	50	28·10	24·1	—	—	95°	55° (Spring)
D'Arcet's . .	50	25·0	25·0	—	—	94°	—
D'Arcet's with mercury . . .	50	25·0	25·0	—	250·0	45°	—
Wood's . . .	50	25·0	12·5	12·5	—	65°	25° (Spring)
Lipowitz's . .	50	26·9	12·78	10·4	—	65°	38·5° („)
Guthrie's 'Eutectic'	50	20·55	21·10	14·03	—	stated to have the lowest melting-point	—

The action of heat on fusible metal is somewhat anomalous. Taking Lipowitz's alloy as a typical example, we find (from Spring's table of densities at different temperatures) that this alloy whilst cooling contracts very rapidly at the solidifying point (65°), contracts slowly from that temperature to 38·5°, expands thence to about 25°, and again contracts, occupying at 0° the same volume as at 46°.

For this reason, in taking a cast or impression with fusible metal, it is advisable to allow the alloy to cool to a pasty mass before placing in the mould (*v.* further, Godefroy, Fremy's Encycl. Chimique, art. 'Bismuth,' 1888, 24–30).

Copper containing small quantities of bismuth is red short. Traces of bismuth are usually present in commercial copper (Field, Chem. News, 36, 261). The two metals unite at a temperature below the melting-point of copper, forming hard, brittle alloys of the mean densities of the constituents (Gelert). An alloy of 1 copper, 2 bismuth expands considerably after solidification; 1 copper, 4 bismuth produces a red crystalline metal.

Antimony unites in all proportions with bismuth. The alloy of equal parts of the two metals expands considerably on solidification.

Mercury dissolves a considerable amount of bismuth without solidifying. The amalgam containing 1 bismuth and 4 mercury adheres strongly to smooth surfaces such as glass. One part bismuth and 2 parts mercury forms a pasty amalgam. The alloy consisting of D'Arcet's alloy and mercury (*v.* preceding table) is used, on account of its low melting-point, for taking casts of anatomical preparations. The alloy is introduced in the liquid state, allowed to solidify, and the fleshy parts dissolved by solution of caustic soda. This alloy is also used for silvering glass tubes, &c.

Silver has a strong affinity for bismuth. An alloy of equal parts of the two metals has the colour of bismuth, is lamellar, and has a density of 10·709, *i.e.* greater than the mean of the constituent metals (Muschenbroeck).

The alloy of *cadmium* 40·8 parts, bismuth 59·2 parts, melts at 144° (Guthrie).

Bismuth alloys with the *alkali metals*; thus, by fusing 5 bismuth with 4 cream of tartar (potassium hydrogen tartrate), an alloy of bismuth and potassium is produced which becomes tarnished in air, has an alkaline reaction and taste, and evolves hydrogen when plunged in water. Johannis (Compt. rend. 114, 585) has obtained an alloy of bismuth and sodium, of the formula $BiNa_3$, by the action of a solution of sodium in

liquid ammonia on bismuth. The compound is of a blue-black colour and takes fire in the air.

A. H. Gallatin (Phil. Mag. [4] 38, 57) has prepared an alloy of bismuth with *ammonium* (?). He scattered ammonium chloride over bismuth sodium alloy, and added water. The alloy swelled and again contracted. On plunging in water or heating, a mixture of hydrogen and ammonia was evolved. After drying *in vacuô* over sulphuric acid, it evolved 27 volumes of gas on heating.

Bismuth combines very imperfectly with iron, forming alloys of diminished density. With platinum, palladium, gold, and tellurium it also forms alloys. Compounds with the two latter metals occur in nature. It is remarkable that the addition to bismuth of as little as 0·05 p.c. of tellurium completely changes the appearance of the metal, which then has a minutely crystalline structure.

Compounds of Bismuth.

Bismuth forms two well-defined classes of compounds, in which it is a diad and a triad respectively. There are indications of the existence of some more highly oxidised compounds, but, assuming their existence to be proved, their constitution can be more easily explained by the assumption of a higher valency for oxygen than by assuming bismuth to be a pentad.

Oxides. Only two oxides of bismuth, the dioxide and the trioxide, are definitely known. The statements of Deichler, Hauser, and Vanino and Treubert, that bismuthic acid and tetroxide exist, have been controverted by Gutbier and Bunz (Zeitsch. anorg. Chem. 48, 162; 49, 432; 50, 210; 52, 124); Moser (Zeitsch. anorg. Chem. 50, 33) states that the addition of hydrogen peroxide to a bismuth salt precipitates only bismuth trioxide. Hollard (Compt. rend. 136, 229) says that a peroxide of the formula Bi_2O_7 is formed during the electrolysis of a solution of bismuth sulphate, but this observation has not been confirmed.

The trioxide and the compounds derived from it are the only ones of commercial importance.

Bismuth trioxide Bi_2O_3 occurs in nature as *bismuth ochre*. It is best prepared by heating the subnitrate of bismuth until red fumes cease to be evolved. It may also be prepared by exposing the metal to a red-white heat in a muffle. The metal then burns and forms the oxide, which condenses as a yellow powder. Bismuth oxide thus obtained is a pale-yellow amorphous substance, which melts at a red heat to a glass without change of weight. Its sp.gr. is 8·21; it contains 89·66 p.c. bismuth.

The oxide can be obtained crystalline, and has been shown to be isodimorphous with antimony trioxide (Muir and Hutchinson, Chem. Soc. Trans. 1889, 143).

It is used for glass and porcelain staining; as an addition to certain fluxes to prevent the production of colour; and in gilding porcelain, being mixed in the proportion of 1 part oxide to 15 parts of the gold.

The darkening of the commercial substance on exposure to light is due to the presence of a trace of silver.

A hydrated bismuth oxide Bi_2O_3,H_2O is precipitated as a white powder on addition of caustic alkali to a bismuthous salt, such as the nitrate; but Thibault (J. Pharm. Chim. 12, 559) has shown that under these conditions the product contains appreciable quantities of oxy-acid salts. By precipitating the hydroxide from an alkaline solution by the addition of acid, a pure product is obtained which on drying yields the pure oxide. It dissolves in alkali in presence of glycerol. On addition of sugar to the solution, metallic bismuth is precipitated, whilst arsenic, if present, remains in solution. Lowe (Zeitsch. anal. Chem. 22, 498–505) recommends this method for the preparation of pure bismuth for pharmaceutical purposes.

Bismuth nitrate $Bi(NO_3)_3,5H_2O$ is prepared by dissolving bismuth or its oxide or carbonate in moderately strong nitric acid. The concentrated solution is filtered, if necessary, through asbestos, and deposits on cooling large deliquescent crystals, which are caustic and melt in their water of crystallisation when gently heated.

When the bismuth used for the preparation contains arsenic, excess of nitric acid should be used for the solution; the arsenic is then oxidised to arsenic acid, and combines with its equivalent of bismuth, being precipitated as arsenate of bismuth. R. Schneider (J. pr. Chem. 20, 418–434) recommends the following proportions: 2 kilos. bismuth, 10 kilos. *hot* nitric acid (75° to 90°); when the action is finished the liquid is decanted from the sediment, which contains all the arsenic. On addition of water to the solution a white precipitate of basic nitrate falls, the constitution of which varies with the amount of water used. This was formerly known as *magistery of bismuth*, and is now called *flake* or *pearl white*, the latter name being also applied to the oxychloride of bismuth.

For pharmaceutical purposes the subnitrate is prepared as follows: Dissolve 2 parts of bismuth in 4 parts nitric acid of sp.gr. 1·42, diluted with 3 parts water, pour from deposit, if any, evaporate to one-third the bulk, and pour into 80 parts of water, filter, wash and dry the precipitate at a temperature not above 55°.

It is a pearly-white powder consisting of minute crystalline scales. It is employed as a flux for certain enamels, augmenting their fusibility without imparting any colour, and on this account is used as a vehicle for metallic oxides. For the colourless iridescent glaze on porcelain the basic nitrate is rubbed with resin and gently heated with lavender oil; by the addition of coloured oxides, yellow and other colours are produced. It is also used like the oxide and in the same proportions for gilding porcelain, and to some extent as a cosmetic under the names *blanc de fard* and *blanc d'Espagne*. It is largely used in medicine.

When prepared from impure metal it is liable to contain arsenic, lead, and silver; tellurium has also been suspected (Pharm. J. 3, No. 287). To test for arsenic, heat a little of the nitrate in a tube until brown fumes cease to be evolved. Add a small crystal of potassium acetate, and again heat; in presence of a trace of arsenic the odour of kakodyl is observed (A. Glenard, J. de Pharm. [4] 1, 217).

Bismuth chloride $BiCl_3$. This compound is produced when finely powdered bismuth is thrown into chlorine gas or when chlorine is passed over the heated metal. It is also formed

by the solution of bismuth in *aqua regia* and evaporation of the liquid; or by distilling a solution of the oxide in hydrochloric acid, changing the receiver when all the water has distilled over.

It is a white, easily fusible solid, which absorbs moisture from the air, forming a crystalline hydrate. By the addition of water a white precipitate of basic chloride or oxychloride is produced corresponding to BiOCl, though its composition varies considerably.

The oxychloride of bismuth is, however, usually prepared by pouring a solution of the normal nitrate into a dilute solution of common salt, forming oxychloride of bismuth and sodium nitrate.

It is a white pearly powder known as *pearl white*, and is used as a pigment, and in the preparation of a very fine yellow pigment known as Merimée's antimony yellow (*v.* ANTIMONY).

Bismuth chromate *v.* under CHROMIUM.

Bismuth sulphite, produced by the action of sulphurous acid on bismuth carbonate, or by double decomposition between a bismuth salt and an alkali sulphite, is a white crystalline powder, and is used in medical practice to check intestinal fermentation, and in cases of worms.

The organic compounds of bismuth have found many applications in medicine and surgery.

Bimsuth salicylate is prepared, according to Causse (Compt. rend. 112, 1220), by adding a solution of a neutral salicylate to a solution of bismuth nitrate in a minimum amount of hydrochloric acid. Considerable quantities of ammonium chloride are added to the solutions before they are mixed. Hydrated bismuth salicylate $Bi(C_7H_5O_3)_3,4H_2O$ is thus obtained as a white crystalline powder, insoluble in cold water.

A better method of preparation, due to Thibault (Bull. Soc. chim. 25, 794), consists in treating the bismuth oxide obtained by precipitation from 15 parts of bismuth nitrate with a solution of 10 parts of salicylic acid in 200 parts of water and heating on the water-bath till the action is complete. The product is decanted, washed with cold alcohol, and dried at 100°. It is thus obtained in rose-grey crystals, which are soluble without decomposition in cold alcohol, ether, or in a saturated aqueous solution of salicylic acid.

Martinotti and Cornelio (Bull. Chim. Pharm. 40, 141) point out that commercial preparations of the salt vary very much in composition, the amount of acid ranging from 5 to 67 p.c., and that of bismuth oxide from 37 to 79 p.c.

Kebler, however, has shown (Pharm. J. 64, 591) that the alcoholic test of the British Pharmacopœia is too stringent, as hot alcohol decomposes the salt. A more trustworthy method of testing of bismuth salicylate for free acid consists in extracting it with 90 p.c. benzene and filtering the extract into dilute ferric chloride solution (1 in 3000), when a violet ring is produced at the junction of the two liquids if free acid is present.

Basic bismuth gallate, known commercially as '*dermatol*,' is prepared as follows: 306 grams of basic bismuth nitrate is dissolved in 328 grams nitric acid of strength 38°B., diluted with 200 grams water. The solution is filtered through glass-wool, evaporated down to 600 grams, and allowed to crystallise. The product is dissolved in 980 grams glacial acetic acid, diluted with 8 litres of water, and then mixed with a solution of 188 grams crystallised gallic acid in 8 litres of water. The precipitate of bismuth gallate thus produced is washed five or six times with water, pressed, and dried (Hartz, Pharm. Rundsch. 12, 182).

Another method consists in treating a solution of bismuth nitrate in nitric acid with a solution of gallic acid in 70 p.c. alcohol, nearly neutralising with sodium hydroxide or sodium carbonate, and finally adding considerable quantities of sodium acetate or diluting largely with water. The compound is thus obtained as a yellow precipitate, which is collected and dried (Eng. Pat. 6234, 1891).

The empirical formula of the substance is $BiC_7H_7O_7$, and Thibault (J. Pharm. Chim. 14, 487) considers that it is really bismuthogallic acid, adducing in favour of this view the fact that with alkalis it forms salts of which potassium bismuthogallate $K_3BiC_7H_5O_7$ is a type.

A general method for the preparation of bismuth salts of organic acids is the solution of freshly precipitated bismuth hydroxide in a solution of the acid (Fischer and Grützner, Arch. Pharm. 1894, 232, 460; *v.* also Telle, *ibid.* 1908, 246, 484, for the preparation of *bismuth lactate* by this method).

Basic bismuth dibromohydroxynaphthoate, which has been suggested as a substitute for iodoform in surgical dressings (G. Richter, Apoth. Zeit. 1908, 23, 600), is obtained by a similar method. β-hydroxynaphthoic acid is brominated in acetic acid solution, and the recrystallised product heated with bismuth hydroxide. The salt is a finely crystalline, yellow, odourless, insoluble powder, which is unaffected by heating to 110°.

Bismuth chrysophanate ('*Dermol*')

$$Bi(C_{15}H_9O_4)_3\cdot Bi_2O_3\ ?\ )$$

a yellowish-brown powder, is, according to Merck, a mixture of impure chrysarobin and bismuth hydrate.

Compounds of bismuth with phenols are obtained by double decomposition between an alkaline salt of the phenol and a salt of bismuth, such as the nitrate. Among those that have been made commercially may be mentioned:

orphol (the β-naphthol compound)

$$C_{10}H_7OBi(OH)_2+Bi_2O_3+H_2O;$$

xeroform (the tribromophenol compound)

$$(C_6H_2Br_3O)_2Bi\cdot OH+Bi_2O_3;$$

helcosol (the pyrogallate)

$$[C_6H_3(OH)_2O]_2\cdot Bi\cdot OH.$$

An important pathological application of bismuth salts is their administration internally in order to outline parts of the body in Röntgen ray work.

Bismuth oxyiodosubgallate $C_6H_2(OH)_3\cdot CO_2\cdot BiI(OH)$, '*airol*,' is prepared by heating together in 50 parts of water 35 parts bismuth oxyiodide, and 18·8 parts gallic acid until the product is a greyish-green powder. It is used as a substitute for iodoform.

Other compounds of bismuth to which trade names have been given are:

Bismal, bismuth methylenedigallate, obtained by the general method from the hydroxide and methylenedigallic acid.

Markasol, bismuth borophenate.

Thioform, bismuth dithiosalicylate, used as substitute for iodoform (*v.* SYNTHETIC DRUGS).

BISMUTHINITE or BISMUTH-GLANCE. Native bismuth sulphide Bi_2S_3, occurring in acicular or bladed orthorhombic crystals or lamellar masses, very like stibnite (Sb_2S_3) in appearance. In Queensland and Bolivia it is found in sufficient abundance to be used as an ore of bismuth. L. J. S.

BISMUTITE. Basic bismuth carbonate, containing about 90 p.c. Bi_2O_3; formula perhaps $Bi_2O_3{\cdot}CO_2{\cdot}H_2O$. It is a yellowish earthy material, and presenting such an appearance is surprisingly heavy (sp.gr. variously given as 6·9 and 7·6). It occurs as an alteration product of native bismuth, and in Bolivia is an important ore of this metal. L. J. S.

BISMUTOSE *v.* SYNTHETIC DRUGS.

BISSA-BOL *v.* GUM RESINS.

BISTRE *v.* PIGMENTS.

BISULPHIDE OF CARBON *v. Carbon disulphide*, art. CARBON.

BITTER ALMOND OIL *v.* BENZALDEHYDE, and OILS, ESSENTIAL.

BITTER APPLE *v.* COLOCYNTH.

BITTER SWEET *v.* DULCAMARA.

BITTER WOOD *v.* QUASSIA.

BITTERN. The mother liquor which remains after the crystallisation of common salt from sea-water, or the water from salt springs. It contains soluble magnesium salts, bromides, and iodides.

The same term is also applied to a mixture of equal parts of quassia extract and sulphate of iron, 2 parts extract of *Cocculus indicus*, 4 parts Spanish liquorice, and 8 parts treacle, used to sophisticate beers.

BITUMEN. This term includes a considerable number of inflammable mineral substances consisting mainly of hydrocarbons. They are of various consistence, from thin fluid to solid, but the solid bitumens are for the most part liquefiable at a moderate heat. The purest kind of fluid bitumen, called naphtha or rock oil, is a colourless liquid of sp.gr. 0·7–0·84, and with a bituminous odour. It often occurs in nature with asphalt and other solid bitumens. Petroleum is a dark-coloured fluid variety containing much naphtha. Maltha or mineral tar is a more viscid variety. The solid bitumens are *asphalt* (*q.v.*); *mineral tallow* or *hatchetin*; *elastic bitumen*, *mineral caoutchouc* or *elaterite*; *ozokerite*, &c.

An abundance of bitumen is found in the island of Trinidad at the Pitch Lakes, and in Mexico. It is supposed to be a product of the decomposition of vegetable matter, and consists chiefly of hydrocarbons with variable quantities of oxygen and nitrogen (*v.* PITCH).

BITUMINOUS COAL *v.* FUEL.

BIXEIN, BIXIN. Colouring matters of annatto (*v.* ANNATTO).

BLACK BAND IRONSTONE *v.* IRON, ORES OF.

BLACK BOY GUM *v.* BALSAMS.

BLACK CHALK. A kind of clay containing carbon, found in Carnarvonshire and in the Isle of Islay.

BLACK COPPER *v.* COPPER.

BLACK EARTHY COBALT *v.* COBALT.

BLACK FLUX *v.* ASSAYING.

BLACKBERRIES. The fruit of the bramble, *Rubus fruticosus*. König gives, as the average composition:

Water	Protein	Free acid	Sugar	Other carbohydrates	Fibre	Ash
86·4	0·5	1·2	4·4	1·8	5·2	0·5

The seeds contain about 12·6 p.c. of a drying oil, sp.gr. at 15° 0·9256, iodine number 147·8, the liquid fatty acids—about 91 p.c. of the oil, contain about 80 p.c. of linolic acid, 17 p.c. of oleic acid, and 3 p.c. of linolenic acid, whilst the solid acids, chiefly palmitic acid, amount to about 4·7 p.c.; volatile acids are not present in the oil. A small quantity of phytosterol is present (Krzizan, Chem. Rev. Fett u. Harz, Ind. 1908, 15, 7). H. I.

BLACK HELLEBORE ROOT. *Radix Hellebori nigri.* (*Racine d'Ellebore noir*, Fr.; *Schwarze Nieswurzel*, Ger.)

The root of the *Helleborus niger* (Linn.) or Christmas Rose (Woodville, Med. Bot. 169; Bentl. a. Trim. 2). Black hellebore and the nearly related green hellebore, *Helleborus viridis* (Linn.), are seldom employed in England except in veterinary medicine. They are both powerful intestinal irritants.

Vauquelin (Ann. de Muséum, 8, 87), Soubeiran (N. Traité de Pharm. 1), and Feneulle and Capron (J. Pharm. Chim. 8, 503) examined hellebore, but no definite constituent of physiological importance was announced till the discovery of *helleborin* by Bastick in 1852 (Pharm. J. 12, 174). Our knowledge of the chemistry of hellebore is, however, chiefly due to Husemann and Marmé (Annalen, 133, 55), who show that besides helleborin, which is a glucoside, there exists in both the black and green hellebore another glucoside, *helleborein*. Helleborein exists in greatest proportion in the *niger*, but it is also the chief of the two constituents in the *viridis*.

Helleborein, when purified, consists of groups of microscopic needles which crumble in the air to a yellowish-white hygroscopic powder. It has a sweet taste and darkens at 220°–230°. Water and alcohol dissolve it, but it is insoluble in ether. Sulphuric acid forms with it a brownish-red solution, which changes to violet. By the action of dilute acids it hydrolyses into *glucose*, and a grey-green amorphous precipitate of *helleboretin*. Helleboretin gives with concentrated nitric acid a violet solution, which deposits violet flakes on pouring into water. Helleborein gives no such colouration (Thaeter, Arch. Pharm. 235, 414). Helleborin likewise assumes the form of white shining needles, and melts with decomposition at 150°. It is insoluble in cold water, slightly soluble in ether, but dissolves easily in boiling alcohol or chloroform. It gives a characteristic and delicate colour reaction with sulphuric acid. The crystals become deep-red and dissolve in the acid to a deep-red solution. The taste of helleborin is acrid and burning. Dilute acids hydrolyse it into *glucose* and a resinous substance, *helleboresin*. Helleboresin is insoluble in water, slightly soluble in ether, but is readily dissolved by boiling alcohol. A. S.

BLACKING. Blacking for shoes is mentioned as early as 1598, but it was not introduced into England until the reign of Charles II. It consists of (1) black bone charcoal (free from calcium phosphate, otherwise it is subsequently treated with dilute sulphuric acid) and black colouring matter; (2) a mixture of sugar and

oil, which, on rubbing, imparts the gloss; and (3) fatty matter for preservation purposes.

A liquid blacking can be prepared from 120 parts of ivory black, 90 parts brown sugar, 15 parts olive oil, and 500 parts stale beer. The ivory black, sugar, and olive oil are mixed into a smooth paste, and the beer added under constant stirring (Hiscox, 1907).

A German recipe is as follows: 25 parts Marseilles soap are dissolved in 375 parts of warm spirit (25 p.c.) and 40 parts of glycerol added; this is shaken and added to a solution of 200 parts of shellac dissolved in 1000 parts of spirit (95 p.c.) and 5 parts nigrosine in 125 parts of spirit added. The mixture is well shaken in a closed vessel and left for a fortnight.

Liquid polish. 4 oz. asphaltum, 8 fl. oz. turpentine, 3 fl. oz. of gold size, ¼ oz. nigrosine, and 3 fl. oz. linseed oil. The mixture is heated until uniform and thinned down to desired consistence with oil of turpentine (Phot. J. Dec. 1908, 738).

Day and Martin's chief blacking is obtained by mixing ground animal charcoal, sperm oil, raw sugar or treacle, and a small portion of vinegar. Dilute sulphuric acid is then added to the mass until intumescence ceases, and the product is thinned by the addition of vinegar.

Bryant and James's indiarubber blacking is prepared by triturating thoroughly 18 oz. very fine shreds of indiarubber, 9 lbs. hot rapeseed oil, 60 lbs. finely powdered animal charcoal, 45 lbs. treacle, 1 lb. gum arabic previously dissolved in 20 gall. vinegar. The whole is placed in a wooden vessel, and 12 lbs. sulphuric acid added in small quantities at a time, and stirred for ½ hour daily for 14 days, 3 lbs. of finely ground gum arabic added, and stirring continued for 14 days. If required in the paste form, only 12 gall. vinegar added and 6 or 7 days' stirring is sufficient.

Brunner makes a blacking by stirring 10 parts of bone black with 100 parts of glucose syrup, and 5 parts sulphuric acid added with rapid stirring until the mass is homogeneous. 2 parts of soda are dissolved in 4 parts water, and 20 parts train oil added and boiled with constant stirring until a thick liquid is formed: the other mixture is then added with repeated stirring.

A cheap and good shoe blacking may be prepared by mixing 1 lb. of ivory black, 1 lb. molasses, 8 tablespoonfuls sweet oil, and 1 oz. of gum arabic, dissolved in 2 quarts of vinegar and ½ lb. of oil of vitriol.

Paste blacking. Mix 16 oz. ivory black, 16 oz. lampblack, 6 oz. treacle, 5 oz. vinegar, and 4 oz. sperm oil. Mix and add gradually 4 oz. sulphuric acid. When intumescence ceases, add ½ oz. of iron sulphate, 6 oz. gum arabic, and 5 oz. water (Pharm. Formulæ, 1908, 378).

Sticks of blacking of plastic consistence are made from the following: 5 oz. stearin, 5 oz. paraffin wax, 2½ oz. carnauba wax, 2½ oz. lustrous pitch, and 7 oz. turpentine (Pharm. J. Pat. 2564, 1908).

Hiscox describes the following paste: 122 parts Marseilles soap, 61 parts potassium carbonate, 500 parts beeswax, and 2000 parts water are mixed with constant stirring and 153 parts rock candy (powdered), 61 parts gum arabic, and 1000 parts ivory black are added with constant stirring.

Boot polish. 5½ oz. ozokerite, 2 lbs. cerasin, 5½ oz. carnauba wax, 1⅜ oz. beeswax, 4 pints turpentine, 2 lbs. lampblack, 20 grams black aniline dye, and perfume added if desired (Pharm. J. 1908, 506).

Self-shining blacking. Dissolve 4 oz. gum arabic, 1½ oz. coarse sugar, ¼ pint good black ink, and 1 oz. sweet oil, rub in a mortar, add 2 oz. strong vinegar, and add lastly 1 oz. rectified spirits (Scientific Amer. 1903, 39).

French shoe dressing. 32 oz. vinegar, 8 oz. logwood, and ½ oz. potassium dichromate are boiled and strained whilst hot into a mixture of 4 oz. gelatine, 4 oz. tragacanth, 4 oz. glycerol and 15 oz. water. The mixture is allowed to stand for some hours: 2 oz. indigo are then added, and the whole triturated in a mortar (Pharm. Form. 1908)

Boot-top liquid. 1 oz. oxalic acid, 1 oz. zinc sulphate, dissolved in 30 oz. water. Apply with a sponge to the leather, which has been previously washed with water, then wash off with water, and dry (Workshop Receipts, 1909, 123).

For kid shoes. 2 oz. gum shellac, 1 oz. aqueous ammonia, 8 oz. water, and aniline black enough to colour. The first two ingredients are heated almost to boiling, and water is added to make the whole measure 16 oz. (Scien. Amer. 1903, 39).

Waterproof blacking. 6 oz. caoutchouc and 3 lbs. hot rape oil are added to 20 lbs. ivory black, 15 lbs. molasses, and 6 or 7 gall. vinegar in which 6 oz. ground gum arabic has been dissolved; then add 4 lbs. sulphuric acid and stir constantly. Allow to stand for 2 weeks, then add 1 lb. fine gum arabic. Stir daily during 2 weeks, and bottle (Workshop Receipts, 1909, 124).

For *dress boots.* 8 oz. gum arabic and 2 oz. molasses dissolved in 2 oz. ink and ¼ pt. vinegar. This is strained, and 2 oz. spirits of wine added.

BLACK JACK. A miner's term for blende, or zinc sulphide (*v.* ZINC).

BLACK LEAD. The common name of plumbago or graphite (*v.* CARBON).

BLACKLEY BLUE *v.* INDULINES.

BLACK LIQUOR. Ferrous acetate (*v.* ACETIC ACID).

BLACK MUSTARD SEED OIL *v.* RAPE OIL: OILS and FATS.

BLACK TELLURIUM *v.* TELLURIUM.

BLACK TIN *v.* TIN.

BLACK VARNISH or **BLACK JAPAN** *v.* VARNISH.

BLACK WAD *v.* MANGANESE.

BLACK, WOOL, *v.* AZO- COLOURING MATTERS.

BLANC FIXE. Trade name for ground barium sulphate, used as a pigment (*v.* BARYTES).

BLANQUETTE. A kind of crude soda, less caustic than barilla, obtained at Aigues-Mortes by the incineration of *Salsola kali.*

BLAST FURNACE GAS *v.* FUEL.

BLASTING GELATINE AND POWDER *v.* EXPLOSIVES.

BLAU or BLUE GAS. A mixture of volatile

hydrocarbons, *e.g.* propane, butane, the pentanes, &c., containing hydrogen and methane, &c., in solution under pressure. The pressure solution is filled into steel cylinders, and is thus available for transport. Used for illuminating heating, and power purposes (Hallock, J. Soc. Chem. Ind. 1908, 550).

BLEACHING. This term signifies the art of destroying the natural colour of vegetable and animal products in such a manner as to leave them unimpaired with as white an appearance as possible. The removal of certain other natural or artificial impurities usually accompanies the bleaching proper. The art acquires its greatest importance in connection with the textile fibres, cotton, linen, wool, and silk; hence special reference will be made to the modern methods of bleaching these materials.

Cotton bleaching. Cotton is usually bleached in the form of yarn, thread, and calico, seldom as loose cotton-wool. The natural impurities occurring in raw cotton amount to about 5 p.c., and consist chiefly of pectic matters; other substances present are brown colouring matter and very minute quantities of a fatty acid, cotton wax, and albuminous matter. The soiled grey appearance of raw cotton-wool, yarn, and thread is almost entirely due to the presence of these natural impurities. Cotton cloth or calico, however, is still further contaminated with flour or starch, fatty matter, China clay, and other mineral substances, all of which, to the amount of 30–50 p.c., have been introduced during the sizing of the warp.

Cotton yarn and thread bleaching. If the cotton yarn is in the form of 'warps,' these are loosely plaited by hand or machine in order to reduce their inconvenient length; if in the form of 'hanks,' these are bleached separately or linked together in chain form; weft yarn is sometimes bleached in the form of 'cops,' *i.e.* ready for the spool of the weaver's shuttle.

The several operations of the bleaching process for 1500 kilos. yarn, employing low pressure kiers, are as follows:—

1. *Ley-boil.* 300 litres caustic soda (sp.gr. 1·16), 2000 litres water, boil 6 hours; wash in kier 1 hour.
2. *Chemicking.* Bleaching-powder solution (sp.gr. 1·005), steep under sieve 2 hours; wash under sieve half an hour.
3. *Souring.* Sulphuric acid (sp.gr. 1·005), steep under sieve half an hour; wash under sieve half an hour and afterwards in washing machine.
4. *Soaping and blueing.* Soap solution about 6 grams per litre, with addition of small quantity of indigo-purple (indigotin monosulphonate of soda), steep 2 hours under sieve.
5. *Dumping.* Pass through dumping machine containing soap solution and indigo-purple, as in operation No. 4; wash, squeeze or hydro-extract, and dry.

The first, second, and third operations are repeated in the case of thread because of its closer texture. For the second ley-boil, 30 litres caustic soda (sp.gr. 1·16) and 15 kilos. soap are used; the chemicking and souring are exact repetitions.

The *ley-boil* takes place in large iron boilers or 'kiers,' a representation of which is shown in Fig. 1.

The boiler A has a central puffer pipe, B, furnished with a bonnet or spreader, M, at the top;

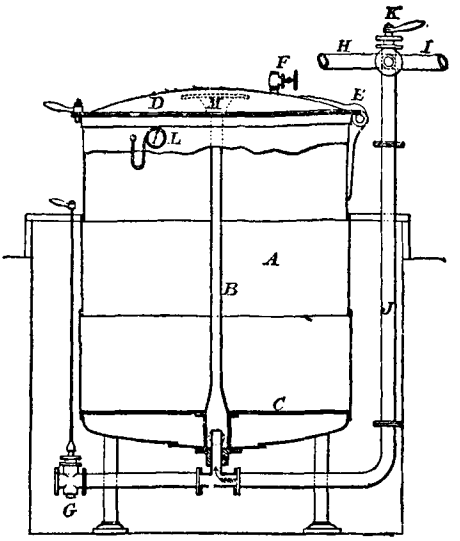


FIG. 1.

C is a perforated false bottom; D is the lid hinged at E and capable of being readily lifted by means of a chain and counterweight; F is an air valve, L a steam pressure gauge; H and I are the steam and liquor pipes connected by the two-way valve K with the pipe J, which enters the kier immediately below the puffer pipe; G is the let-off valve.

When such a kier has been charged with yarn and caustic soda solution, the lid is fastened down and steam is admitted. The liquor below the false bottom soon begins to boil, and as the pressure of steam increases, a portion of the boiling liquor is forcibly ejected up the puffer pipe and spread over the yarn. The liquor drains through the yarn, soon to be ejected as before. In this intermittent manner the circulation of the boiling liquor is maintained.

The apparatus for chemicking, souring, washing under sieve, soaping and blueing, shown in Fig. 2, consists of a stone tank, E, with perforated false bottom F, and communicating by the valve G with the stone tank D below. The chain of yarn is drawn from the kier and led into the tank E by means of the winch A. When E is suitably filled with yarn, the liquor in tank D is raised by the pump C to the sieve F', whence it drains through the yarn into the well below, again to be pumped up as before; B is the eccentric wheel on revolving shaft by which the pump is worked.

The 'dumping' machine referred to consists of a pair of heavy wooden rollers placed over a large wooden tank containing the soap solution. The upper roller is covered with cotton rope and rests loosely on the lower one. The yarn is first passed through the soap solution and then between the squeezing rollers; the irregularities caused by the linking or plaiting impart to the upper roller a constant jumping motion, which

thus effectually cleanses the yarn and presses the soap and blue into the fibres.

When hank yarn is not linked to form a chain, but treated as separate hanks, 'wash stocks' in which the yarn is subjected to the beating action of heavy wooden hammers, replace the dumping machine.

Bleaching of yarn in the form of 'cops' or 'cross-wound spools' ('cheeses'). The cops may be packed in wicker baskets or in linen bags and boiled in an ordinary kier, or they are treated in special cop-dyeing apparatus. It is preferable to use a solution of sodium hypochlorite in place of a bleaching-powder solution.

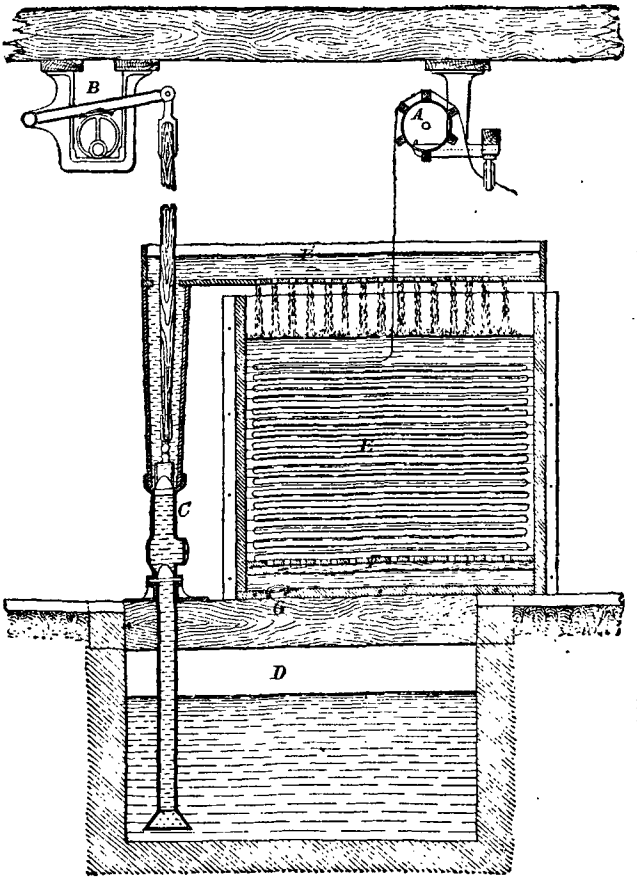


FIG. 2.

Cotton-cloth or calico bleaching. According to the purpose for which the bleached material is intended, we may distinguish between the *madder bleach*, the *market bleach*, and the *Turkey-red bleach*.

The madder bleach. This, the most thorough kind of calico bleaching, is in general use with calico-printers. It aims at entirely removing every impurity which will attract colouring matter in the madder or other dye-bath, so that the finished print may have a pure white ground.

Before proceeding to the actual bleaching process the preliminary operations of *stamping*, *stitching*, and *singeing* have to be performed.

To recognise each piece of cloth and to trace damages, the ends are stamped with numbers and letters, usually with thick gas tar, occasionally with aniline black. The pieces are then stitched together by machine.

The *singeing* operation is for the purpose of burning off the loose fibres on the surface of the calico, since they interfere with the production of fine impressions, and are apt to give rise to certain defects during the printing process. It is performed by rapidly passing the cloth in the open width over red-hot copper plates or cylinders, or over a row of Bunsen gas flames. We may distinguish, therefore, between *plate singeing* and *gas singeing*, the former being generally preferred for thick heavy cloth, the latter for light thin cloth, muslins, &c.

In plate singeing it is important that the plates be kept at a uniform strong red heat sufficiently high to overcome the cooling action of the rapidly moving cloth. The best results are obtained by means of the 'singeing roller,' which consists of a slowly revolving copper cylinder through which a furnace flame is conducted. In this case the cloth presses continually against a different portion of the red-hot surface of the roller; the cooling action is thus reduced to a minimum, and a regular even singe is the result.

All singeing machines are provided with lever arrangements for immediately removing the cloth from the hot plate, or the gas flame from the cloth, in case of necessity; further danger from fire is avoided by causing the singed cloth to pass at once between a pair of rollers moistened with water, or through a small steam chamber, in order to extinguish sparks adhering to the cloth.

The above preliminary operations are now succeeded by those of the bleaching proper. The following is an outline of the process at present in use for 24,000 kilos. cloth, employing low-pressure kiers:—

1. Wash after singeing.
2. *Lime-boil.* 1000 kilos. lime, water about 37,000 litres; boil 12 hours; wash.
3. *Lime sour or grey-sour.* Pass through hydrochloric acid (sp.gr. 1·01); wash.
4. *Ley-boils.* 1st. 340 kilos, soda ash, water about 37,000 litres; boil 3 hours.
   2nd. 860 kilos. soda ash, 380 kilos. resin, 190 kilos. caustic soda (solid), water 37,000 litres; boil 12 hours.

3rd. 380 kilos. soda ash, water 37,000 litres; boil 3 hours; wash.

5. *Chemicking.* Pass through bleaching-powder solution (sp.gr. 1·0025); pile 2–12 hours; wash.

6. *White-sour.* Pass through hydrochloric or sulphuric acid (sp.gr. 1·01); pile 1–3 hours.

7. Wash, squeeze, open out, and dry.

1. *Wash after singeing.* From the singeing house the cloth is passed through the washing machine in rope form, then plaited down on the floor and allowed to lie 'in pile' for some hours to soften. By this operation the cloth is well soaked with water, and is thus better prepared to absorb the liquors used in the subsequent operations. Should the cloth be heavily sized, much of the adventitious matter is also removed at this stage.

The form of washing machine generally employed is shown in Figs. 3 and 4. It consists of a water trough, B, above which a pair of heavy wooden squeezing rollers, A, A, are supported. Two strands of cloth are washed simultaneously; they enter the machine at the ends, pass between the squeezing rollers, then round the roller R in the water trough, again between the rollers A, A, and thus travel spirally towards the centre of the machine, whence they are drawn out by a winch and piled on the floor. A constant stream of water from the main G enters at the centre of the trough by the tap E, the dirty water flowing out at both ends; C, C are wooden guide pegs to separate the several

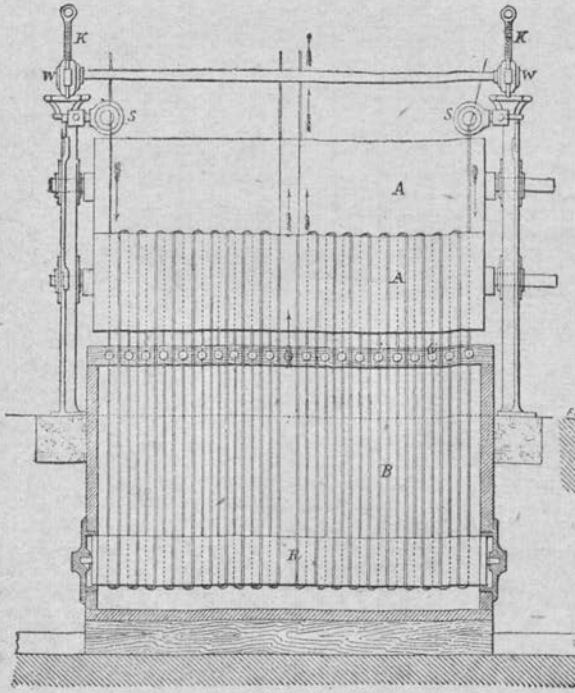


FIG. 3.

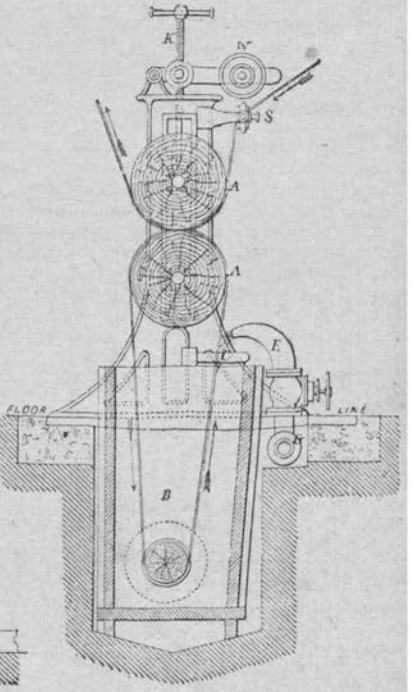


FIG. 4.

strands of cloth; S, S are strong brass rings or 'pot eyes' through which the cloth enters the machine, and which can be set at any angle to regulate its tension; K and W are the screws, levers, and weights for regulating the pressure of the squeezing rollers against each other. The action of this machine is such that the cloth is continuously being soaked with water and then squeezed, thus causing a vigorous stream of water to flow down the upward-moving strands of cloth.

2. *Lime-boil* (lime-bowk, bucking, bowking). The pieces are run through milk of lime supplied to a washing machine of small dimensions—generally termed the 'liming machine'—and are at once drawn by winches into the lime kiers, carrying with them the lime they have absorbed. The cloth is plaited in regular folds and well tramped down by boys, who enter the kiers. After adding the necessary amount of water, the boiling and circulation of the liquor takes place as already described in the case of the ley-boil of cotton-yarn bleaching.

The lime-boil has for its object the decomposition of the fatty, waxy, and resinous impurities present in the cloth. Though not removed, but adhering still to the fabric in the form of lime-soaps, their altered condition facilitates their removal by the subsequent processes. The starch of the size is removed, and the colouring matter of the fibre is modified. Lime is preferred to caustic soda because it is cheaper, and much more effective in saponifying neutral fatty matter than the caustic or carbonated alkalis; indeed, with the exception of barium hydroxide, it seems to be the most energetic saponifying agent which could be used in cotton bleaching.

It is very essential to have a sufficiency of water in the kier, so that it stands at least about 2 feet above the false bottom; otherwise the cloth, either at the top or bottom of the kier, is very apt to be tendered, probably because it becomes oxidised by the action of the steam upon the cloth in its limed condition. On the other hand, an excess of water in the kier is to be avoided, since then the cloth is apt to float and become entangled, or damaged by rubbing against the sides of the kier during the boiling. When closed high-pressure kiers and live steam are employed, the increase in volume of liquor by the condensation of the steam must be taken into account, and, if necessary, a little liquor must be allowed to escape.

Of the several varieties of kier which have from time to time been introduced in practice, mention may be made of '*Barlow's kiers.*' These are always worked in pairs, and so arranged that the top of one kier is connected by a pipe with the bottom of the other; the pipes which enter at the top and centre of each kier are continued as perforated pipes or 'distributors' to a little above the false bottom, and then to the bottom of the kier as a stay. Both kiers having been charged with cloth, the necessary amount of water is run into one kier only; high-pressure steam is then admitted at the top, and the liquor forced out below enters the distributor of the other kier at the top and permeates the cloth. When all the liquor has been thus transferred, the taps are reversed so that the steam forces the liquor in a similar manner back into the first kier. This alternating process and circulation of the liquor is continued for about seven hours.

Pendlebury's arrangement of kiers is precisely similar to that of Barlow, the only difference being that one kier is smaller and serves only to hold the liquor each time it is forced through the cloth contained in the larger kier. The arrangement is cheaper, more economical as regards space required, and is suitable for small requirements.

In the *vacuum kier* of Mason and others, the circulation of the liquors is effected by means of a pump. After filling the kier with cloth, the air is pumped out and the boiling liquor is then admitted; in this manner a more perfect penetration of the material by the liquor is obtained.

The *injector kier* of Mather and Platt is shown in Fig. 5. A is the kier filled with cloth; B, B are the steam pipes; C is the injector; and D the circulating pipe; F is the liquor pipe by which water or other liquor is admitted; E, E is the draw-off valve and waste pipe. When the kier has been suitably filled with cloth and liquor, steam is turned on, and, by the action of the injector C, the liquid is withdrawn from the kier below, forced up the pipe D, and spread over the cloth at G. Temporarily collecting at H, the liquor is gradually drawn through the cloth, and in this manner a continual circulation of liquor is maintained.

3. *Lime-sour* (grey-sour). After the lime-boil the pieces are washed, then passed through a washing machine fed with dilute hydrochloric acid, and, if convenient, at once washed.

The object of the lime-sour is to decompose the insoluble lime-soaps fixed on the cloth during the lime-boil, and to dissolve and remove the lime, also any iron or other metallic oxides present. Experiments by A. Scheurer show also that the use of the lime-sour makes it less essential that complete saponification of the fatty matter should take place during the lime-boil than would be the case if it were omitted. This is so because the free fatty acid liberated during the lime-sour greatly facilitates the saponification of any undecomposed neutral fat during the succeeding ley-boil, since the soap which the fatty acid then forms emulsifies the neutral fat and exposes it to the action of the alkali employed. Hence the adoption of the lime-sour is equivalent to shortening the time of the lime-boil. A continual flow of fresh dilute acid into the machine must be maintained, and, since it is rapidly neutralised by the lime, it is well to ensure a constant slight acidity of the liquor by occasionally making acidimetrical tests. Hydrochloric acid is preferred to sulphuric acid, because it gives the more soluble calcium chloride. The soured cloth should never be permitted to remain long exposed to air, especially air currents, otherwise the acid is apt to concentrate in the exposed portions and thus tender the fibre.

4. *Ley-boil.* This operation takes place in the same kind of kiers as are used for the lime-boil. The fatty acids resulting from the decomposition of the lime-soaps during the grey-sour, also the brown colouring matters, are removed during this operation. Its special feature is the use of resin-soap, which greatly facilitates the removal of fatty matter by exercising a purely mechanical emulsive action, the alkali present being then able more readily to saponify the emulsified fats, particularly those neutral fats which perchance have escaped the action of the lime-boil. Ordinary soft-soap acts in a similar manner, but resin-soap is cheaper and better. A. Scheurer finds by experiment that, after caustic lime, the most rapid saponification of a neutral fat spotted on a piece of calico is effected when boiling under pressure at 120° C., by a solution containing 10 grams anhydrous caustic soda and 2½ grams resin per litre. Increasing the amount of resin does not hasten saponification, though this is done by increasing the velocity of the circulation of the solution. Indeed, *with circulation* even a more rapid saponification is effected with caustic soda and resin than with lime.

The preliminary short boiling with soda ash, which is sometimes replaced by merely soaking the cloth in a weak solution of soda ('sweetening'), prevents tendering of the cloth by neutralising any traces of acid left in by reason of insufficient washing after souring. The boiling with soda-ash after the resin-boil is for the purpose of completing the removal of fatty matters and any undissolved resin, which otherwise give rise to brown stains. Immediate removal of the cloth from the kier and washing is necessary to prevent the production of iron stains.

5. *Chemicking.* The application of the bleaching-powder solution takes place in washing machines of the ordinary kind, but provided with stone instead of wooden troughs, because of their greater durability. The bleaching action takes place essentially during the lying-in-pile

or exposure to air of the cloth saturated with the solution of bleaching powder; the carbonic acid of the air liberates hypochlorous acid, and this, in the presence of the fibre, at once decomposes, yielding hydrochloric acid and oxygen: in the moment of its production the oxygen oxidises and destroys the traces of colouring matter present in the fibre, thus giving it the highest degree of whiteness.

It is necessary to avoid the use of strong solutions of bleaching powder, otherwise the fibre itself is attacked, oxycellulose being produced; and even if the cotton is not tendered thereby it is still apt to acquire brown stains during subsequent operations employed by the calico-printer, *e.g.* steaming, or to produce uneven shades in dyeing.

6. *White-sour.* This operation is similar to the lime-sour already described, except that sulphuric acid is usually employed instead of hydrochloric acid, chiefly because of its lower cost. Its object is to decompose and remove traces of undecomposed bleaching powder, lime, iron, and the oxidised colouring matter.

7. The *final washing* must be as thorough as possible in order to ensure the removal of all traces of acid, which, if left in the cloth, would inevitably tender portions of it during the drying process. After washing, the cloth is specially squeezed by passing through a pair of heavy wooden rollers, or through the modern grooved brass roller and disc machine of W. Birch. The chain of cloth then passes in a horizontal, loosely hanging position, between a pair of rapidly revolving, double-armed winches or scutchers, which effectually shake out the twist from the strand. Thus opened out to the full width, the cloth is dried by passing over steam-heated copper cylinders, and folded. The time usually required to complete the madder bleach is four to five days.

The market bleach. In market bleaching the object is simply to give a brilliant white appearance to the calico or other similar material, to fit them for immediate sale in the market as finished white goods. It is not necessary to have the calico well 'bottomed'—*i.e.* cleansed from all colour-attracting impurities, since no subsequent dyeing or printing is intended. The operations are for the most part identical with those of the madder bleaching process. The modifications introduced are shown in the following outline of the process, intended for 24,000 kilos. cloth, employing open or low-pressure kiers:—

1. *Lime-boil.* 1440 kilos. lime, water about 37,000 litres; boil 12 hours; wash.
2. *Lime-sour.* Hydrochloric acid (sp.gr. 1·01); steep 2–4 hours; wash.
3. *First ley-boil or grey-boil.* 240 kilos. caustic soda (solid), about 37,000 litres water; boil 12 hours; wash.
4. *Chemicking.* Bleaching-powder solution (sp.gr. 1·005); steep 2–4 hours; wash.
5. *Second ley-boil or white-boil.* 240 kilos. soda ash, about 37,000 litres water; boil 12 hours; wash.
6. *White-sour.* Sulphuric acid (sp.gr. 1·01); steep 2–4 hours; wash.
7. *Tint* with blue; squeeze dry.

More or less elaborate finishing operations follow—*e.g.* starching, calendering, beetling, stentering, &c. Some bleachers introduce a white-sour between operations 4 and 5, and a second chemicking between operations 5 and 6. The absence of resin-soap in the ley-boils is characteristic.

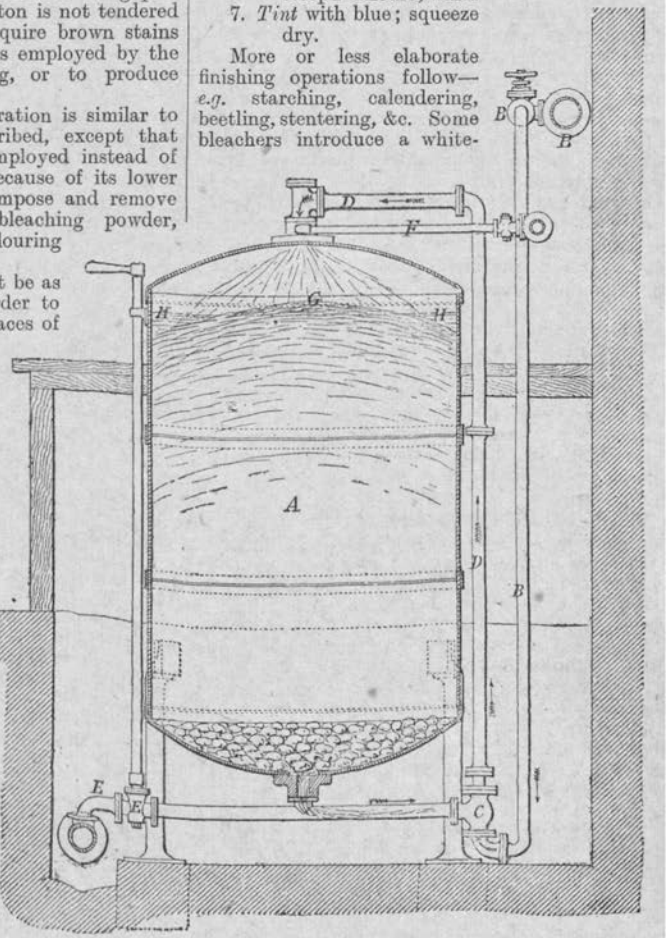


FIG. 5.

The Turkey-red bleach. This is merely a curtailment of the foregoing processes, and is specially intended for yarn or cloth to be subsequently dyed plain alizarin-red or Turkey-red. In it the operation of singeing and the application of bleaching powder are omitted, since they diminish the fulness and brilliancy of the Turkey-red dye; the use of the latter is to be avoided, because it gives rise to the production

of oxycellulose. The use of resin-soap is unnecessary, and the process is limited to the following operations :—

1. Wash.
2. Boil in water 2 hours ; wash.
3. *Ley-boils.*
   - 1st. 90 litres caustic soda (sp.gr. 1·35), about 3000 litres water ; boil 10 hours ; wash.
   - 2nd. 70 litres caustic soda (sp. gr. 1·35) ; ditto, ditto.
4. *Sour.* Sulphuric acid (sp.gr. 1·01) ; steep 2 hours.
5. Wash well and dry.

The above quantities of materials are intended for 2000 kilos. cloth, with low-pressure kier.

The steamer-kier bleaching process. The bleaching processes previously described have been in vogue with little change during the last forty years ; minor modifications have certainly been introduced, but the chief improvements have always been in respect of the mechanical appliances employed.

In 1883 Thompson patented a bleaching process in which the goods contained in an air-tight kier are submitted to the action of bleaching-powder solution and of carbonic acid alternately.

In 1884 W. Mather, of the firm of Mather & Platt, Manchester, devised an improved arrangement in which the calico could be passed continuously through chambers or tanks containing the two necessary agents mentioned.

The so-called *Mather-Thompson* process results from a combination of the two processes here indicated. With regard to the principles of the process there is nothing new, for the application of carbonic acid in connection with bleaching-powder solution was patented by P. F. Didot in 1855, while the steaming of goods impregnated with alkali was patented as far back as 1800 by J. Turnbull.

The novelty consists essentially in the machinery employed, by which the duration of the bleaching process is very much shortened, and other material advantages are gained.

In the following year Mather introduced the

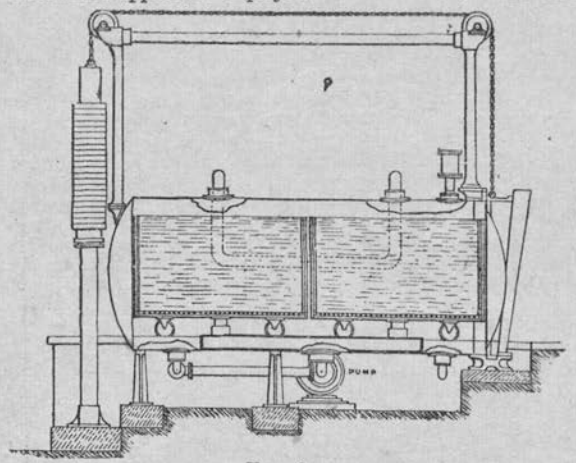


FIG. 6.

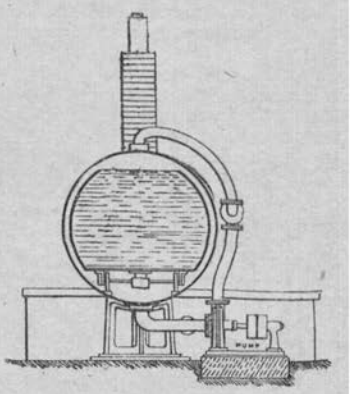


FIG. 7.

so-called *steamer-kier*, in which the goods, previously impregnated with dilute caustic soda, were submitted to the action of low-pressure steam.

The steamer-kier consists of a strong wrought-iron horizontal boiler, one end of which can be closed by a specially constructed sliding door. At the side of the kier stands a centrifugal pump connected with the top and bottom of the kier, and also with liquor tanks beneath, so that either boiling water or dilute caustic alkali solution can be sprinkled on and circulated through the goods. Figs. 6 and 7 show the general disposition of the steamer-kier.

Two waggons of cloth having been run into the kier, and the door closed, steam is admitted till the pressure reaches a maximum of 4–5 lbs. During the steaming or boiling process, a continual sprinkling of the cloth with dilute caustic soda (sp.gr. 1·01–1·02) is maintained, in order to keep the cloth well saturated with liquid, and thus prevent oxidation and consequent tendering of the fibre by the action of the steam. The excellent circulation of the liquors in the steamer-kier is a noteworthy and most important feature, since it greatly facilitates the saponification of the fatty matters on the cotton.

After steaming, the liquor is run off, the kier is almost filled with hot water, and this is circulated through the cloth by means of the centrifugal pump for one hour. A similar washing with fresh hot water takes place during another hour.

Each kier is provided with two pairs of waggons, so that while the goods in one pair are being steamed, the other pair can be emptied and refilled with cloth ready to be steamed. In this manner the operation of steaming is rendered as continuous as possible and a very great saving of time is effected.

The following details have been furnished by H. Koechlin, of the Loerrach Printworks :—

To effect the *madder bleach* by the *steamer-kier* process, the continuous bleach with the application of carbonic acid, &c., is omitted, the older method of chemicking and souring being preferred. Those who consider the lime-boil as essential may apply it equally well by means of the steamer-kier.

The operations in this case are as follows :—

1. *Lime-boil (or steam).* Run through milk of lime, 50 grams per litre, and pile in steamer-waggon ; boil in steamer-kier 5 hours at 10 lbs. pressure, circulating 2000 litres water. Wash in kier with hot water.
2. *Sour.* Sour as usual with dilute HCl (sp.gr. 1·015) ; pile 2–3 hours, and wash.
3. *Ley-prepare.* Pass through NaOH solution (sp.gr. 1·005–1·01), heated to 70° C., and pile in steamer-waggon.
4. *Ley-boil (or steam).* Boil 6 hours in steamer-kier at 10 lbs. pressure, with circulation of resin-soap liquor : 40 kilos. soda ash, 20 kilos. resin, 1000 litres water. Wash four times (½–1 hour each time) with boiling water, and finally with cold water, in kier.
5. *Chemicking.* Pass as usual through dilute bleaching-powder solution (sp.gr. 1·0025) ; wash.
6. *Sour.* Pass as usual through dilute sulphuric acid (sp.gr. 1·01) ; wash and dry.

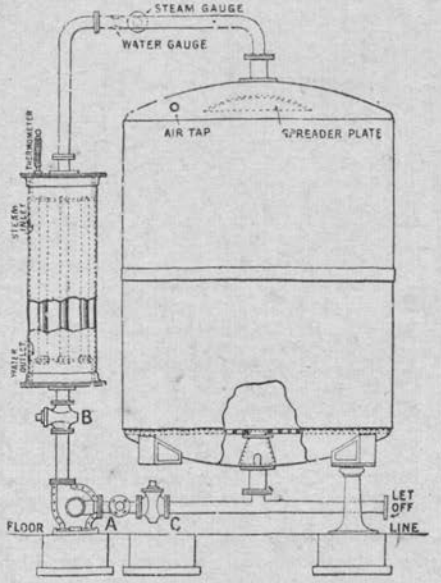


FIG. 8.

Perfectly satisfactory results, however, are obtained by even *omitting* the lime-boil and proceeding as follows :—

1. *Sour.* Pass as usual through dilute H_2SO_4 (sp.gr. 1·015) ; pile 2–3 hours ; wash and squeeze.
2. *Ley-prepare.* Pass through following solution at 70° C. : 20 litres bisulphite of soda (sp.gr. 1·3), 20 kilos. NaOH (solid 72 p.c.), 1800 litres water ; pile in steamer-waggons.
3. *Ley-boil (or steam).* Boil in steamer-kier 6–8 hours at 10 lbs. pressure, with circulation of resin-soap liquor : 20 kilos. NaOH (solid 72 p.c.), 40 kilos. soda ash, 20 kilos. resin, 2000 litres water ; wash 4 times (½–1 hour each time) with boiling water, and once with cold water in kier.
4. *Chemicking.* As above.
5. *Sour.* As above ; wash and dry.

With the exception of the employment of the steamer-kier and the use of bisulphite of soda, this process is essentially the same as that employed for many years with success by Messrs. Guillaume Frères of St. Denis.

The preliminary souring process effects the decomposition of any insoluble fatty acid compounds present in the grey cloth ; it removes calcareous or other mineral matter soluble in acids, and modifies any starchy matter present, probably rendering it more soluble. The addition of the small proportion of the reducing agent bisulphite of soda, along with the caustic soda in the preparing process, is intended to prevent any oxidation and consequent tendering of the cotton during the steaming process. The use of resin-soap along with the caustic soda, combined with the perfect circulation of the liquor, is very material to the success of this method of madder bleaching, for reasons already stated.

According to H. Koechlin, this method gives a perfectly satisfactory bleach. The white is not permanently stained in an alizarin dye-bath, and does not become yellow on steaming.

A noteworthy invention of Dr. G. Lunge is the application of acetic acid in connection with bleaching powder, in place of mineral acids or carbonic acid. It can be applied immediately before or after, or even along with, the solution of bleaching powder. It liberates hypochlorous acid with formation of soluble calcium acetate. When the hypochlorous acid exercises its bleaching power, it gives up oxygen

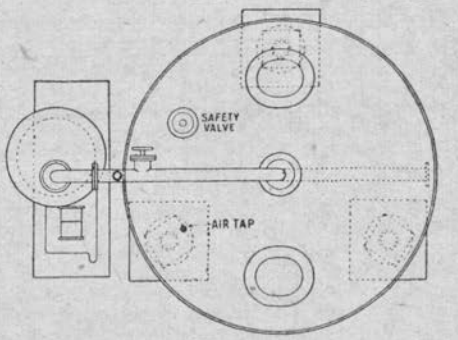


FIG. 9.

and produces hydrochloric acid, which immediately acts upon the calcium acetate. In this manner the acetic acid is reproduced, and is thus ready to decompose fresh portions of calcium hypochlorite.

Hadfield and Sumner patented a process in which the cloth, after having been impregnated with a solution of bleaching powder, is passed through a box containing acetic acid vapour.

A solution of sulphurous acid has been used by some bleachers for the final souring process in place of sulphuric acid, over which it possesses the advantage of being an antichlor, in consequence of its reducing action.

The Walsh kier. In this kier, shown in Figs. 8 and 9, which is very largely used, the boiling

liquor is circulated by means of a centrifugal pump, and it is heated in a special heating arrangement outside the boiling kier.

In the *Bentz-Edmeston* and in the *Tagliani-Rigamonti* kiers the boiling operation is a continuous process. Low pressure is usually employed, and the impregnation of the pieces with the boiling liquor in the lower part of the kiers is followed by steaming in the upper part. After the boiling is completed the pieces are plaited into wooden boxes, in which they are allowed to lie for some hours.

Piece goods, such as heavy twills, &c., which are frequently damaged (creased) in ordinary bleaching in the rope form, are treated in the open width. Special kiers have been constructed for this purpose, the principal one being the *Jackson-Hunt* kier (Fig. 10).

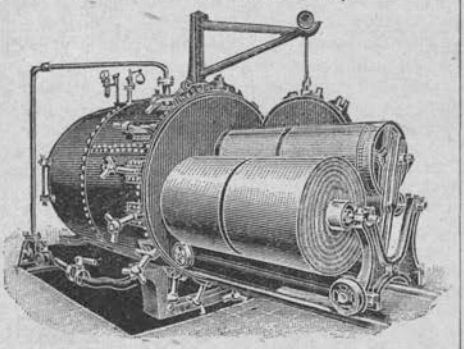


FIG. 10.

Previous to boiling in this kier the cloth is impregnated with caustic soda ley, which has been used in a former boiling, in a special batching machine. In this the cloth travels over a perforated drum, and the soda ley is forced through it by means of steam, which is blown against it whilst it travels over the drum. Ultimately, the cloth is wound tightly and evenly into a batch.

This batch is now placed on a waggon, which is transferred to the horizontal boiling kier.

Special driving gear is provided, by means of which the cloth is wound off the batch on to another batching roller, passing over a heavy perforated drum which rests on both batches. The caustic soda liquor is circulated by means of a centrifugal pump, and is showered over the cloth during its passage over the perforated drum.

In this kier the cloth is usually boiled under high pressure (about 45 lbs.).

In the preparation of *sodium hypochlorite* solution, by electrolysing a solution of common salt two types of processes are employed, one in which the products of electrolysis, viz. sodium and chlorine, are not allowed to combine, and the other in which they are allowed to combine to form sodium hypochlorite

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$

The latter process comes chiefly into consideration as regards the bleaching of textile materials.

The apparatus used may be divided into two classes, the one in which electrodes made of platinum-iridium are used, and the other in which carbon electrodes (highly compressed graphite) are employed.

In the Kellner electrolyser, which belongs to the former kind, a centrifugal pump is employed by means of which the salt solution is repeatedly passed through the apparatus until it contains from 3 to 5 grams of active chlorine per litre.

In the Haas and Oettel electrolyser, which belongs to the latter kind, the salt solution is electrolysed until it contains from 10 to 15 grams of active chlorine per litre.

Powerful circulation of the salt solution is obtained by means of the hydrogen gas evolved during electrolysing.

Bleaching by means of electrolytically prepared hypochlorite solution, although employed with advantage in special cases, such as the bleaching of cops, is not commonly practised, because it is more expensive in its application than bleaching powder.

The statement that an electrolytically prepared bleaching solution is more effective than a solution of bleaching powder containing the same amount of active chlorine, cannot be confirmed in practice.

Permanganate of potash, *sodium peroxide*, and *hydrogen peroxide* give excellent results in bleaching. Their price, as compared with bleaching powder, is, however, in most instances, prohibitive.

The history of cotton bleaching may be briefly said to comprise the following noteworthy improvements :—

1. The use of chlorine gas by Berthollet in 1787, and of hypochlorite of lime in 1799 by Tennant.
2. The boiling with carbonate of soda instead of caustic soda, after the lime-boil, introduced from America about 1837. A more effectual decomposition of the lime-soaps was thus obtained.
3. The adoption of the lime-sour, as proposed by A. Scheurer-Rott in 1837.
4. The use of resin-soap in the ley-boils about the same period.
5. The introduction of high-pressure boiling kiers about 1844.
6. The use of caustic alkali and resin-soap in conjunction with the steamer-kier, to the exclusion of the lime-boil, in 1883–84.

Linen bleaching. Since the retted flax fibre contains a much larger proportion of natural impurities than cotton, *e.g.* 25–30 p.c. of pectic acid, beside fatty matter, &c., linen is not so readily bleached as cotton. In the main, however, the methods adopted for the two fibres are the same. Linen is bleached in the form of yarn, thread, or cloth.

Linen-yarn bleaching. Very frequently linen yarn is only partially bleached, the process being completed, if necessary, when the yarn has been woven into cloth.

The following operations are employed in order to obtain 'half-white' or cream, with 1500 kilos. yarn, using low-pressure kiers :

1. *Ley-boil.* Boil 3–4 hours in a solution of 150 kilos. soda ash ; wash and squeeze.
2. *Chemick* (*reel*). Reel 1 hour in bleaching-powder solution, sp.gr. 1·0025 ; wash.
3. *Sour.* Steep 1 hour in dilute sulphuric acid, sp.gr. 1·005 ; wash.

4. *Ley-boil (scald).* Boil 1 hour in a solution of 30–75 kilos. soda ash; wash.
5. *Chemick.* Reel in a dilute solution of bleaching powder, sp.gr. 1·0025; wash.
6. *Sour.* Steep 1 hour in dilute sulphuric acid, sp.gr. 1·005; wash well and dry.

If the yarn should be bleached more completely, then operations 4, 5, and 6 are repeated two or three times, as may be found necessary, with this difference, that between 4 and 5 the yarn is 'grassed,' *i.e.* exposed in the field to the action of the air, light, and moisture, for several days. By introducing this very gentle method of bleaching, the full strength of the fibre is better maintained.

The various operations are conducted in apparatus precisely similar to that employed in the bleaching of cotton yarn, except in the operation of chemicking. Although steeping under the sieve in dilute bleaching-powder solution might well be employed, it is usual to suspend the hanks of linen yarn on reels in such a manner that they are only partially immersed in the solution contained in a shallow tank. As the reels revolve the yarn becomes thus alternately impregnated with the solution and exposed to the air. The liberation of hypochlorous acid by the carbonic acid of the air is advantageous, and the bleach is more effective and regular.

The application of acetic acid, as proposed by Lunge, instead of this exposure to air, may here be strongly recommended, since then no insoluble lime salt is fixed on the fibre, and the subsequent souring is reduced to a minimum.

To avoid the presence of caustic lime, some bleachers use hypochlorite of magnesia, as proposed by Hodge, instead of bleaching powder.

Linen-cloth bleaching. The old method of bleaching linen cloth consisted in alternately boiling the fabric with solutions of sodium carbonate and exposing on the grass, succeeded by souring, and rubbing with solutions of soap. The modern method, adapted from that employed for calico, is given in the following *résumé*. It is intended for 1500 kilos. brown linen, using low-pressure kiers.—

1. *Lime-boil.* Boil 14 hours with 125 kilos. lime, 2000 litres water; wash.
2. *Sour.* Steep 2–6 hours in dilute hydrochloric acid, sp.gr. 1·0025; wash in stocks, *turn-hank*, wash.
3. *Ley-boils.* First, boil 8–10 hours with 2000 litres water containing resin-soap; 30 kilos. caustic soda (solid), 30 kilos. resin, previously boiled together with water; secondly, boil 6–7 hours with 2000 litres water, 15 kilos. caustic soda (solid), previously dissolved; wash.
4. *Expose in field* 2–7 days according to the weather.
5. *Chemick.* Steep 4–6 hours in dilute bleaching-powder solution, sp.gr. 1·0025; wash.
6. *Sour.* Steep 2–3 hours in dilute sulphuric acid, sp.gr. 1·005; wash.
7. *Ley-boil (scald).* Boil 4–5 hours with 2000 litres water, 8–13 kilos. caustic soda (solid); wash.
8. *Expose in field* 2–4 days.
9. *Chemick.* Steep 3–5 hours in dilute bleaching-powder solution, sp.gr. 1·0013; wash.

At this stage the cloth is examined; those pieces which are sufficiently bleached are soured and washed, the rest are further treated as follows:—

10. *Rub* with rubbing boards and a solution of soft soap.
11. *Expose in field* 2–4 days.
12. *Chemick.* Steep 2–4 hours in dilute bleaching-powder solution, sp.gr. 1·0006; wash.
13. *Sour.* Steep 2–3 hours in dilute sulphuric acid, sp.gr. 1·005.
14. Wash, squeeze, and dry.

If the linen is not brown, but made of yarn already partly bleached, the above process is much curtailed, and weaker liquors are employed.

The kiers, chemicking and souring machines are the same as those used in cotton-cloth bleaching. The washing is done in the so-called wash-stocks or by slack-washing machines. The latter are very similar to the cotton-washing machines, the chief difference being that the water tank is divided into compartments, each of which holds a few yards of slack cloth forming each strand, before it passes through the squeezing rollers.

The 'rubbing' referred to is for the purpose of removing mechanically any remaining brown particles of ligneous matter termed 'sprits.' It consists in passing the chain of cloth through a solution of soap, and then immediately between a pair of horizontal, corrugated, heavy boards; the upper board rests loosely upon the lower one, and moves lengthwise to and fro, while the pieces pass between them at right angles.

The operation of 'turn-hanking' consists in disentangling the pieces after they have been washed in the stocks, and then refolding them for a further wash, thus ensuring a thorough cleansing of every portion of the cloth. When slack-washing machines are employed, the operation is of course not necessary.

The chemistry of linen bleaching is essentially the same as that of bleaching cotton. The pectic acid, fatty matters, &c., are rendered soluble by the alkaline boilings, and the colouring matters still remaining are oxidised and destroyed by hypochlorites. The repetition of these operations is considered necessary by reason of the large percentage of impurities present; but it is very probable that good results would be obtained by adopting the more rational plan of first removing the whole of the pectic and fatty matters before applying the hypochlorites.

A process of boiling linen goods preparatory to the bleaching has been patented by Cross and Parkes. The pieces are first impregnated with a solution of soap, silicate of soda, caustic soda, and mineral oil. They are then wound on a batching roller in a chamber containing steam, and afterwards steamed for some hours. This is followed by boiling with a solution of silicate of soda or of soda ash. The goods are finally washed; they are now ready for the first 'dip.'

Wool scouring and bleaching. The bleaching of wool never forms a separate industry, as in the case of cotton and linen, and, although in itself of minor importance, it is necessarily preceded by the operation of 'scouring,' which is of fundamental importance both to the woollen manufacturer and the dyer.

In its natural condition the wool fibre is

contaminated with 15–80 p.c. of foreign matter, consisting partly of dirt, &c., derived from without, but mainly of certain fatty matters designated as 'yolk,' secreted by the animal from which it is derived. This secretion is separable into two parts—the one, 'wool-perspiration,' is soluble in water, and consists essentially of the potassium compounds of oleic and stearic acids (potash soaps), &c.; the other portion, termed 'wool-fat,' is insoluble in water, and is composed of cholesterol and iso-cholesterol, which exists partly in the free state, but chiefly in combination with oleic acid and other fatty acids.

Loose-wool scouring. The object of scouring wool is to remove from it the yolk, &c., and thus render it more suitable for spinning, dyeing, or bleaching. Two methods of effecting it may be employed. The one generally adopted is to treat the wool with dilute alkaline solutions capable of forming emulsions with the yolk; the other mode is to submit the wool to the successive action of fat solvents, carbon disulphide, &c., and of water.

Scouring with alkaline solutions. When carried out in the most complete manner, this method comprises the following operations:—

1. *Steep* several hours in tepid water.
2. *Scour* 15–30 minutes with dilute alkaline solutions (soap, sodium carbonate, &c.) at about 50° C.
3. *Wash* with water.

The *steeping* is performed in a series of large iron tanks, in which the wool is systematically washed or rather steeped in water heated to 45° C., until it is deprived of soluble matter. As a rule, two or three steeps with fresh water are found sufficient; but it is customary to pass the wash-water through several lots of wool until it becomes well saturated with 'wool-perspiration.' It is particularly advantageous in the case of wools rich in yolk (*e.g.* Buenos Ayres wool, &c.), since it prevents too rapid soiling of the scouring bath and consequent staining of the wool, and thus it tends to ensure more complete scouring. By evaporating the waste steeping liquors to dryness, and calcining the residue, a good quality of potassium carbonate, containing very little sodium salts and suitable for glass manufacturers, is obtained.

The *scouring and washing* of the wool in order to remove the remaining 'wool-fat' is best performed by the aid of so-called wool-scouring machines, one of which (J. & W. McNaught's) is shown in Fig. 11.

It consists of a large rectangular trough, A, with a light frame, B, suspended over it by chains and carrying a series of transverse, fixed, vertical rakes or combs, C.

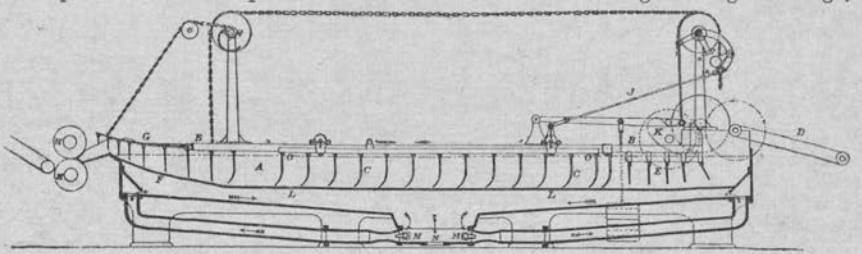


FIG. 11.

The wool, either in its raw condition or after steeping, is spread evenly on the moving endless apron or feeder D; it is thus continuously introduced at one end of the trough.

By suitable mechanism the frame is lowered, and the wool is at once pressed beneath the surface of the scouring liquor by the perforated tray or sieve E. When the frame is sufficiently lowered, it moves forward, the rakes gently carrying the wool towards the other end of the trough. When the forward stroke is completed, the frame is lifted up, the rakes rise vertically out of the liquid, and the frame returns to its original position. By these successive movements the wool is slowly passed through the scouring liquor. At the delivery end it is carried up the inclined plane F by the rakes fixed on the small frame G, which is hinged to the larger one. Having been pushed over the ridge, the wool slips down between the squeezing rollers H, H, ready to be passed through a second similar machine.

The working of the machine as above described, is suitable for Botany and other fine classes of wool. When washing low Cape, River Plate, and similar wools, which contain much dirt and sand, an additional movement is given to the rakes while in the liquor. This is effected by having the rakes fixed in a second frame, OO, which receives a slight backward-and-forward movement by means of the rod O and the cam K during the inward movement of the main frame BB, to which it is attached. By this means the wool is slightly opened out and agitated, and the sand and dirt fall through the perforated grating LL. When the scouring liquor becomes too soiled for further use, the steam injectors MM are brought into action in order to stir up all sediment, and the dirty liquor is run off by the plug-hole N.

For a complete arrangement there should be at least three such machines placed in line, so that the wool passes automatically from one to the other. The first contains more or less soiled scouring liquid which has been previously used in the second trough; the second contains fresh scouring liquid; and the third a continual flow of clean, cold, or preferably tepid water.

The choice of scouring agents depends upon the character and quality of the wool. For fine lustrous wools and such as are poor in yolk, a mild scouring agent should be selected, *e.g.* soap, ammonia, ammonium carbonate, 'lant,' &c., that is to say, agents which are capable of removing the yolk with the least injury to the fibre. The best soaps to use are those which are most soluble and least likely to contain any trace of caustic or carbonated potash or soda.

Should these injurious constituents be present, the soap solution may be de-alkalised by the addition of a small quantity of boracic acid or ammonium chloride, thus yielding the less injurious alkali borates and ammonia, respectively.

Potash soaps, being very apt to contain excess of alkali, should be critically examined. An excellent and very soluble soap may be readily made from oleic acid and caustic soda.

Although a perfectly neutral soap does not always effect a rapid and complete removal of yolk, still it is better to adopt it, since one can always add the proper quantity of other agents, *e.g.* sodium carbonate, ammonia, &c., when necessary.

For low-class wools containing a large proportion of yolk, and when cheapness is a desideratum, sufficiently satisfactory results are obtained by the proper use of sodium carbonate free from caustic soda or other injurious impurity. Suitable sodium carbonates are sold under such commercial names as refined soda ash, Solvay soda, concentrated crystal soda (Brunner, Mond, & Co.), crystal carbonate (Gaskell, Deacon, & Co.), &c.

It is impossible to give precise data with respect to the concentration and temperature of the scouring solution to be employed, since these vary somewhat according to the character of the wool operated upon. If the best results are to be obtained, the solutions must always be applied as dilute and at as low a temperature (not above 50° C.) as is consistent with the complete removal of the yolk.

The waste scouring liquors are collected in large tanks and neutralised with sulphuric acid; the liberated fatty acids are sold to oil refiners, who by distillation obtain purer products, suitable for making soap.

Scouring with volatile liquids. This method is still only in an experimental stage. Mechanical difficulties, the fear of fire and explosions, the first cost of the scouring agent, &c., seem to have prevented the general adoption of this process. Its advantages are that the wool-fat is more completely removed than by the emulsion method, and the wool itself is not injured. A certain degree of success has been obtained by the method proposed by T. J. Mullings, and tried on a large scale. It consists in submitting the wool to the action of carbon disulphide in a closed centrifugal machine until the whole of the wool-fat is dissolved, then expelling the solvent by means of water, and not as heretofore by heat or steam, which always leaves the wool with a yellow colour. The wool must afterwards be washed in warm water to remove wool-perspiration and other impurities. The wool cleansed in this manner is said to be stronger, capable of spinning finer yarn and with less waste and at less cost than if scoured by the ordinary method with soap.

The same principle is adopted in the process of Singer & Judell of Adelaide, who employ, however, a more elaborate and more perfect apparatus, whereby the scouring is made continuous. The raw wool is placed on a feeding apron and carried along between two broad endless bands of wire gauze, first through a succession of fourteen tanks containing carbon disulphide and then through five containing water, all suitably enclosed. The wool, still held between the wire gauze bands, then passes between hot rollers in a steam-heated drying chamber and emerges in a scoured, washed, and dried condition. Arrangements for automatically collecting the dirt which settles from the carbon disulphide, for separating the latter from the water, distilling and returning it to the scouring tanks with the least possible loss, are all provided for by ingenious devices, and the general arrangement seems eminently typical of the method of scouring wool to be adopted in the future. It is said to have been worked with success in Australia.

Woollen-yarn scouring. The object of scouring woollen yarn is to remove the oil with which wool has been impregnated by the spinner. Precisely the same agents are used as for loose wool, but the machinery employed is necessarily different.

Those yarns which have a tendency to curl up because they have been highly twisted are submitted to the preliminary operation of 'stretching'; it also prevents them from shrinking during the subsequent scouring process.

The hanks of yarn are suspended on the arms of a strong iron frame and tightly stretched by means of screws. Thus charged, the frame is immersed in boiling water for a few minutes. After changing the position of the hanks on the arms, the operation is repeated, the yarn is allowed to cool in the stretched condition, and is then removed ready for scouring.

The scouring of yarn is effected either by hand or by machine. In the first case the hanks of yarn are suspended on wooden rods placed across a rectangular steam-heated tank containing the scouring liquor. During a period of 15 to 20 minutes the rods are swayed to and fro by hand, one by one, each hank being frequently turned in order to expose every portion to the action of the liquor. The yarn is washed in another tank in the same manner.

Yarn-scouring machines are to be met with in several forms. A very effective one consists of a rectangular tank, C, having several rollers above and below, and a pair of squeezing rollers, A, B, situated at one end. The hanks of yarn, linked together by means of string loops, are passed continuously through the scouring liquor,

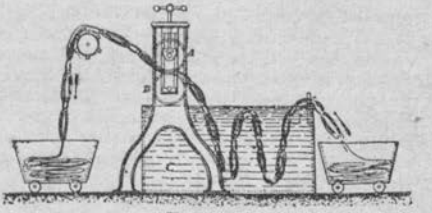


FIG. 12.

and are then washed in a similar machine (*see* Fig. 12).

Woollen-cloth scouring. Woollen cloth is also scoured for the purpose of removing the oil with which the yarn is impregnated by the spinner. The operation consists in passing the cloth as an endless band, either in the strand form or in the open width, through the scouring liquor and then through a pair of squeezing rollers.

For thick woollen cloths, flannels, &c., scouring in the strand is preferred, since a certain

amount of felting takes place and the cloth acquires a better handle. For worsted goods and such as are liable to crease, scouring in the open width is preferable.

Fig. 13 shows a section of E. Kempe's machine for this purpose. It consists of two

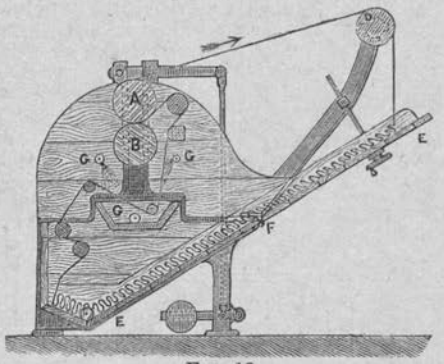


FIG. 13.

squeezing rollers, A and B, placed above the wooden trough C containing the scouring liquor. The roller D serves to draw the cloth from the squeezing rollers, and causes it to fall in regular folds upon the inclined plane EE. This is covered with corrugated zinc, the grooves of which run longitudinally, in order to reduce the friction of the cloth, and to prevent the latter from moving to either side. The upper part of the inclined plane is hinged at F, so that the inclination of this part can be regulated to suit different qualities of cloth, and to ensure that it always slips down in regular folds without any tendency to fall over or become blocked. The perforated water-pipes G, G are for the purpose of washing the cloth after scouring.

Bleaching of wool. After scouring, the wool still possesses a faint yellow tint, to remove which is the object of the bleaching proper. The agent almost universally employed is sulphur dioxide, either in the form of gas (gas-bleaching) or in solution (liquid-bleaching). With hydrogen peroxide a more permanent white is obtained, but it is still too expensive to admit of extended application, but it serves as an excellent bleaching agent for certain fine materials.

Gas-bleaching, stoving, or sulphuring, consists in exposing the scoured and washed woollen material, while still wet, to the action of sulphur dioxide in a brick chamber. Yarn or thick cloth is suspended on poles, the sulphur (6–8 p.c. on the weight of wool) contained in an iron pot is ignited, the chamber door is closed, and the material is then left exposed to the action of the gas for six or eight hours, or even overnight. Thin cloth is generally passed in a continuous manner through a similar chamber provided with rollers above and below. The cloth in the open width enters through a narrow slit at one end of the chamber; it passes in a zigzag course under and over the rollers to the further end, then returns and passes out by the same slit. The sulphur dioxide is prepared in the stove itself, or it is produced in a separate furnace and led beneath the perforated floor of the chamber. According to the appearance of the fabric, it is passed through the bleaching chamber once or several times. Fig. 14 gives a sectional view of the sulphur stove for the continuous bleaching of cloth.

In **liquid-bleaching** the woollen material is immersed and moved about for several hours in a solution of sulphurous acid, or in one containing sodium bisulphite, and acidified with sulphuric acid. One may also steep the wool, first in a solution of sodium bisulphite and then in dilute sulphuric acid, and repeat the operations as often as may be necessary. The liquid-bleaching process has not met with that general acceptance to which it seems entitled.

After bleaching, the materials are well washed and tinted blue or bluish-violet, *e.g.* with refined indigo, indigo-extract, aniline-blue, methyl violet, &c., in order to counteract the yellowish tint which is so liable to return.

The bleaching action of sulphurous acid is most probably due to its reducing properties. According to this view, the sulphurous acid takes up oxygen from the water present, while the liberated hydrogen combines with the colouring matter of the wool to form a colourless leuco-compound. Another explanation, however, is that a colourless sulphurous acid compound is formed. Frequent washing of the wool with alkaline solutions restores the yellow colour. It seems evident, however, that the yellowing influence of alkalis is largely due to their further action upon the wool substance itself since they cause the wool eventually to become yellower than it was before bleaching.

Bleaching with hydrogen peroxide is effected by steeping the wool for several hours in more or less dilute solutions of this liquid, made slightly alkaline by the addition of ammonia. The simultaneous action of light accelerates and improves the bleaching. The white is very good and permanent, probably because, in this case, the colouring matter is destroyed by oxidation. Excessive bleaching by this method gives the wool a harsh feel. Lunge recommends a slight treatment with hydrogen peroxide of sulphur-bleached wool in order to oxidise and thus render innocuous traces of sulphurous acid not removed by washing. A very dilute solution of sodium hypochlorite and exposure to air will effect the same purpose.

Bleaching of wool with hydrosulphite of soda has been suggested by F. V. Kallab. It is prepared by adding zinc powder to a solution of bisulphite of soda. The zinc is precipitated by adding milk of lime.

Silk scouring and bleaching. The raw silk fibre consists essentially of two substances, *fibroïne* and *sericine*. The former constitutes the central portion of the fibre, and may be regarded as the fibre proper, while the latter resides principally in the external part and is readily removed by water and especially alkaline solutions.

Raw silk is harsh, stiff, lustreless, and more or less unsuitable for dyeing, but when the external sericine or silk-glue is removed it becomes soft and lustrous, and acquires an increased affinity for colouring matters.

The object then of scouring is to remove the silk-glue from the raw silk. It is effected by the two operations, '*stripping*' and '*boiling-off*.'

Stripping or ungumming. In order to remove calcareous or other mineral matter soluble

in dilute acids, it is well first to rinse the silk in a tepid bath of dilute hydrochloric acid, and then wash. The hanks of silk are then hung on smooth wooden rods and worked, as in woollen-yarn scouring, in a soap-bath heated to about 90°–95° C. for about 20 minutes. A second and even a third bath may be used with advantage. Long working in one bath is not good, especially for silk intended to be white, since the silk (fibroïne) is apt to attract some of the colouring matter at first removed along with the silk-glue, and it is afterwards very difficult to remove. With yellow silk this point must be carefully attended to.

During the stripping operation the sericine at first swells up and makes the silk somewhat glutinous, but soon it dissolves off and leaves the fibre soft and lustrous. The waste soapy liquors, strongly impregnated with sericine, are carefully preserved and find an important use in silk-dyeing under the name of '*boiled-off liquor*.' When applying the coal-tar colours, it serves to retard their attraction by the silk, and thus ensures the production of even or level colours.

After stripping the silk is rinsed in water containing a small proportion of soap and sodium carbonate.

Boiling-off. The object of this operation is to complete the removal of the silk-glue and thus give the silk all the lustre and brilliancy of which it is capable. The hanks of silk are tied up in coarse bags of cotton or hemp, generally called 'pockets,' and these are boiled for one to three hours in open copper boilers. The silk is then well rinsed in a weak tepid solution of carbonate of soda, and finally in cold water.

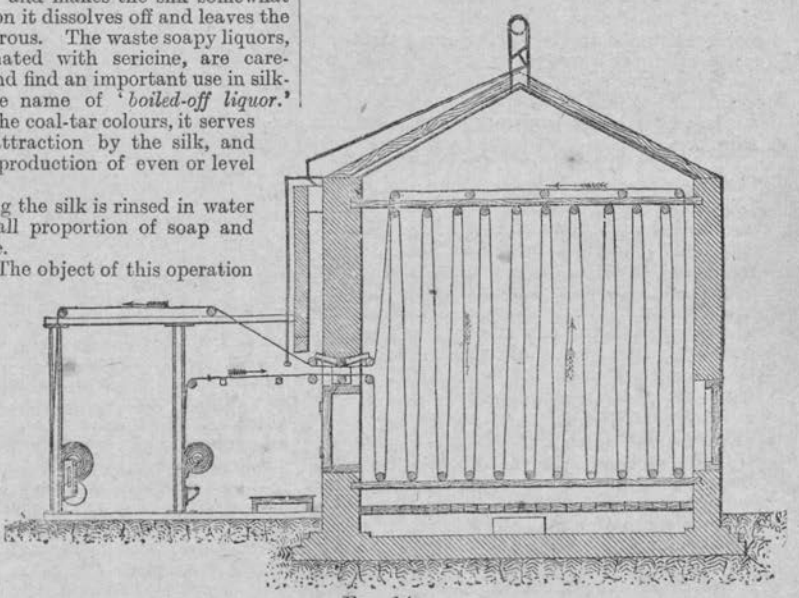


FIG. 14.

During the operations above described, Japanese and Chinese silks lose 18–22 p.c. in weight, European silks lose 25–30 p.c.

Bleaching of silk. The actual bleaching of silk is effected by exposing the scoured silk, while still in the wet state, to the action of sulphur dioxide gas. The operation is precisely similar to the stoving of wool.

In certain cases, *e.g.* with so-called 'souple' silk, the stoving is preceded by a preliminary bleaching in *aqua regia*, diluted to sp.gr. 1·02 and heated to 20°–35° C. The silk is rinsed in this solution for 8–15 minutes until it acquires a greenish-grey colour, and then at once washed well in cold water. A dilute solution of the so-called 'chamber-crystals' of the sulphuric acid manufacture may replace the *aqua regia*.

The bleaching of silk with hydrogen peroxide is gradually being more and more adopted, especially for Tussur silk and other wild silks. Indeed, for these silks no other method of bleaching is so satisfactory. The silk is steeped and worked in a dilute solution of hydrogen peroxide, rendered slightly alkaline with ammonia or with silicate of soda or borax, until it is sufficiently bleached. A more rapid and effective method is to steep the silk in a somewhat stronger solution, then wring out the excess of liquid, and steam. The operations may be repeated until the silk is sufficiently bleached.

Tinting of silk. Bleached silk is finally tinted or dyed in delicate shades of blue, purplish-blue, cream colour, &c. For pure white it is usual to dye the silk in a very dilute solution of a suitable coal-tar colour. After tinting, the silk is slightly rinsed in water and dried in a moderately warm and darkened stove. J. Hü.

BLEACHING POWDER *v.* CHLORINE.

BLENDE, from *Blenden*, Ger., to dazzle. Native zinc sulphide. It usually contains iron sulphide which gives it a black colour, whence the name Black Jack applied to it. An important ore of zinc. The sulphur it contains is occasionally utilised in the manufacture of sulphuric acid. (For descriptions of burners for this purpose, *v.* J. Soc. Chem. Ind. 3, 631; 4, 54.)

BLEU DIRECT or **DIPHENYLAMINE BLUE** *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU FLUORESCENT $C_{18}H_3Br_8N_2O_5(NH_4)$. A colouring matter obtained by Weselsky and Benedikt in 1880 by treating diazoresorufin dissolved in potassium carbonate with bromine and precipitating by an acid. Soluble in boiling water with a red-violet colour, giving a fluorescent green solution. Dyes silk and wool blue with brownish fluorescence (Weselsky and Benedikt, Monatsh. 5, 605; Ber. 1885, 18; Ref. 76).

BLEU DE GARANCE. Artificial ultramarine (*v.* ULTRAMARINE; PIGMENTS).

BLEU LUMIÈRE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU DE LYON, BLEU DE NUIT, BLEU DE PARIS *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU MARIN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU DE SAXE *v.* COBALT.

BLEU SOLUBLE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLIND-COAL. A Scotch term for anthracite.

BLISTER STEEL *v.* IRON.

BLOCK FUEL *v.* FUEL; also PITCH.

BLOCK TIN *v.* TIN.

BLOOD is a richly albuminous fluid which holds in suspension large numbers of corpuscles. The fluid medium in which the corpuscles float is called the plasma, or *liquor sanguinis*. In round figures, the plasma contains about 10 p.c. of solids, of which proteins comprise 8, extractives 1, and inorganic salts (the principal one being sodium chloride) the remaining 1. The proteins are all coagulable by heat, and are named serum albumin, serum globulin, and fibrinogen. The last-named is the least abundant (0·4 p.c.), but confers upon the blood its characteristic power to clot or coagulate when it is shed. When shed, the blood rapidly becomes viscous, and then sets into a jelly; the jelly contracts and squeezes out of the clot a straw-coloured fluid called serum, in which the shrunken clot then floats. The formation of threads of a solid protein called fibrin from fibrinogen is the essential act in coagulation; this with the corpuscles it entangles constitutes the clot, and serum is plasma *minus* the fibrin which it yields. The following scheme shows the relationships of the constituents of the blood at a glance:—

$$\text{Blood}\begin{cases}\text{plasma}\begin{cases}\text{serum}\\ \text{fibrin}\end{cases}\\ \text{corpuscles}\end{cases}\text{clot.}$$

In round figures, the blood contains 60–65 p.c. of plasma, and 35–40 p.c. of corpuscles. The corpuscles are of three kinds, the red corpuscles or erythrocytes, the white or colourless corpuscles or leucocytes, and some very small particles also colourless, which are called the blood-platelets.

The subject of blood clotting has been the battlefield of numerous opposing theories, but the view now generally held is that the conversion of fibrinogen into fibrin is due to the action of an enzyme called thrombin or fibrin-ferment. This agent takes origin from the platelets and white corpuscles; it is first shed out from them in an inactive form called thrombogen; thrombogen is converted into the active enzyme thrombin by the combined action of the calcium salts of the plasma and of an activating agent termed thrombokinase, which originates from the cells of the blood itself and of the other tissues of the body.

The white or colourless corpuscles are typical nucleated animal cells which have been differentiated into varieties by their staining reactions, the number of their nuclei, and their seat of origin (lymphoid tissue, and red bone marrow). Their most important property is their power of amœboid movement, by which they ingest and subsequently digest foreign particles. They act in this way as scavengers (phagocytes), and thus confer protection against pathogenic organisms (bacteria, &c.).

The red corpuscles are much more numerous than the white, averaging in man 5,000,000 per cubic millimetre, or 400–500 red to each white corpuscle. It is these which give the red colour to the blood. They vary in size and structure in different groups of the vertebrates. In mammals they are biconcave (except in the camel tribe, where they are biconvex) non-nucleated discs, in man $\frac{1}{3200}$ inch in diameter; during fœtal life nucleated red corpuscles are, however, found. In birds, reptiles, amphibia, and fishes, they are biconvex oval discs with a nucleus; they are largest among the amphibians. Their most important and abundant constituent is the pigment hæmoglobin. In invertebrates this respiratory pigment is usually absent, and when present is, with few exceptions, in solution in the plasma and not in special corpuscles. In other invertebrates its place is taken by other respiratory pigments, for instance, by the green pigment which contains iron and is called chlorocruorin (in certain worms), or by the blue pigment which contains copper and is termed hæmocyanin (in certain crustaceans and molluscs). The vast majority of invertebrates have colourless blood containing only colourless corpuscles. Hæmoglobin contains 0·4 p.c. of iron; it and certain of its derivatives give characteristic absorption spectra which form one of the best tests for blood. It is termed a conjugated protein, consisting of a protein (globin) in combination with the iron containing material termed hæmatin

$$(C_{32}H_{30}N_4FeO_3)$$

Hæmoglobin is crystallisable, but hæmatin has not yet been obtained in crystalline form. By boiling dried blood with a little sodium chloride and glacial acetic acid, the characteristic brown crystals of hæmatin hydrochloride or hæmin are readily obtained, and this is the best chemical test for blood; it can be performed quite readily on a microscope slide. By treatment with acid, an iron-free derivative of hæmatin is obtained called hæmatoporphyrin, and in the body certain iron-free derivatives somewhat similar to hæmatoporphyrin are formed; these constitute the pigments of the bile. By the reduction of hæmatoporphyrin, methylpropylpyrrol is obtained, and the same substance is obtained also from phylloporphyrin, a derivative of chlorophyll; this is an interesting fact, as it indicates a near relationship between the principal pigments of the animal and vegetable worlds.

During life the blood is in constant movement (circulation), and it is owing to this circumstance that it supplies the tissues with both nutriment and oxygen. The products of protein and carbohydrate digestion pass directly from the alimentary canal into the blood-vessels; the fat reaches the blood indirectly by the lymph-stream. The blood, however, does not, except in the spleen, actually bathe the tissue elements; the middle-man between blood and tissues is a fluid called lymph, which exudes from the blood through the thin walls of the capillary blood-vessels. The lymph thus supplies the tissues with material for their repair or for storage; it also removes from the tissues the waste products of their activity; it is collected by lymphatic vessels, which converge to the main lymphatic channel called the thoracic duct. This opens into the large veins near to their entrance into the heart, and thus the lymph is

returned to the blood, and the waste products are then conveyed to the various organs (lungs, kidneys, skin) by which they are discharged from the body.

The function of blood as an oxygen carrier is dependent on the presence of hæmoglobin. Oxygen passes by diffusion into the blood of the lungs, and is then seized by the pigment, with which it forms a loose compound called oxyhæmoglobin; this bright-red arterial or oxygenated blood passes to the heart, and is thence propelled by the arteries all over the body; in the tissues, where the oxygen tension is very low, oxyhæmoglobin is dissociated, and the oxygen passes into the plasma, and again reaches the actual tissue elements *viâ* the lymph. The reduction of oxyhæmoglobin changes the colour of the blood to the darker tint which it has in the veins, by which vessels it is carried back to the heart and sent to the lungs for a fresh supply of oxygen. The venous blood is also rich in carbonic acid, which finds an exit from the blood in the lungs into the expired air. It should be noted that hæmoglobin is not the carrier of carbon dioxide; that gas is carried mainly as carbonates in the blood-plasma.

The amount of respiratory oxygen carried by the blood pigment is 1·34 c.c. oxygen per gram of hæmoglobin. This can be replaced by equivalent amounts of such gases as carbon monoxide or nitric oxide. These compounds are more stable than oxyhæmoglobin, and the gas is not removable by the tissues; hence in coal-gas poisoning the colour of the blood is equally bright in arteries and veins, and the cause of death is oxygen starvation.

The foregoing outline of the composition and uses of the blood from the physiological point of view can be amplified by the study of any standard textbook of physiology or physiological chemistry.

Passing now to the technical and commercial aspect of the case, the uses of the blood come mainly under four headings: (1) as food; (2) as manure; (3) as a clarifying agent; and (4) as a drug.

(1) As *food*. Blood as such is only used as food by savages, and attempts have been made to utilise dried defibrinated blood as a commercial food product without any great success. It, however, forms an important constituent of certain articles of diet, of which Black pudding and the German Blutwurst (Blood sausage) are the best known. In the preparation of these pig's blood is most commonly employed, and they are of high nutritive value. (For the composition of various kinds of Blutwurst, *see* König, Chemie d. menschl, Nahrungs und Genussmittel, Berlin, 1904, 525; Pott. Handb. d. Tier-Ernahrung, iii. 513, 1909; E. Schmidt, Lehrb. d. pharm. Chem. ii. 2, 1833, 1901.)

(2) As *manure*. Dried blood, the so-called Blood-meal (Blutmehl), is extensively used as manure, and may be placed directly on the land, or, more frequently, is mixed with superphosphates. It is a brown powder with a glue-like smell, and must be kept in dry places to avoid putrefaction. It is valuable on account of its high percentage of nitrogen (11·8) and of phosphorus (1·2 p.c.). Numerous patent manures contain a certain proportion of blood. (For details, *see* König, *l.c.* 496; Merck's Waren-Lexicon, 5th ed. art. 'Blut.')

(3) As *a clarifying agent*. Blood is employed in the same way as milk, gelatin, and albumin are, as a clarifying agent for wines, syrups, and similar liquids, in the proportion of 150–200 c.c. of blood per litre. The clearing action is due to the proteins present, but used in this way there is considerable danger of infection, as also is the case for milk. Dried blood or the dried blood-albumin is therefore preferable. Blood-albumin is prepared from the serum drained off from the clot; the product is really dried serum, as the proteins are mixed with the other constituents of that fluid, and the word 'albumin' is used as synonymous with 'protein,' and not in the correct chemical sense. It has the advantage of being considerably cheaper than egg-albumin, for the total blood of an ox will yield 750–800 grams of the dried product, a good-sized calf will yield 340–400 grams, and a sheep about 200 grams (*see* Merck, *l.c.* art. 'Blutalbumin').

(4) *The therapeutic uses of blood and serum*. The high nutritive value of blood makes it a valuable drug in the treatment of anæmia, and certain patent medicines sold under the name of hæmatogen consist very largely of blood mixed with suitable flavouring and preservative agents. A still larger practical use of blood products (serum therapy) has been the outcome of work on immunity, in which the names of Richet, Ehrlich, Behring, and Roux may be mentioned as those of pioneers. Those interested in problems of immunity should consult current handbooks of pathology. The following does not pretend to do more than give a sketch of the main facts, and the example selected of the usefulness of the method is that in which serum therapy has been the most successful, namely, the treatment of diphtheria. The animal body is protected against its foes by a variety of mechanisms, and against our microscopic (bacterial) enemies the most potent of these is the action of colourless blood corpuscles (phagocytosis). This, however, is assisted in certain cases by the presence in the fluid part of the blood of chemical substances which have received a variety of names; for instance, 'bacteriolysins' are substances which actually kill bacteria; 'agglutinins' are substances which clump the bacteria together and render them immobile; 'opsonins' are substances which render bacteria an easy prey to leucocytes, either by adding something to them to make them tasty or removing something from them which makes them distasteful; and 'antitoxins' are substances which neutralise the poisons or toxins which are produced by the bacteria. There is very little accurate chemical knowledge of the composition of these various materials; they are, however, as a rule, destroyed by a high temperature, and are probably protein-like in nature. The amount of these substances in the blood may be increased by certain stimuli, much in the same way as the epidermis becomes thickened as the result of manual labour. The administration, for instance, of small doses of the toxin will produce an excessive production of the antitoxin which specifically neutralises the poison. Substances which in this way stimulate the production of these natural antidotes are spoken of in general terms as antigens.

If the bacilli which produce diphtheria are grown in a suitable medium, they produce the diphtheria toxin much in the same way as yeast will produce alcohol when grown in a solution of sugar. If a certain small dose of this poison is injected into an animal, it will produce death, and that is called the lethal dose. But if the animal receives a smaller dose, it will recover; a few days later it will stand a larger dose and recover more quickly; this is continued until after many successively increasing doses, it will finally withstand without ill effects an amount equal to many lethal doses. The animal is now immune against diphtheria, for the administration of the toxin (or antigen) has called forth an excessive production of antitoxin, and the blood remains rich in antitoxin for a considerable but variable time; the serum obtained from the blood of the immunised animal is then employed for injecting into other animals or human beings suffering from diphtheria, and rapidly cures the disease. The horse is the animal selected for the preparation of antitoxin, and the success of the new treatment in reducing the death-rate from what used to be considered a terrible disease is one of the wonders of modern medicine.

(5) *Miscellaneous uses of blood.* Blood is, or has been, employed in a number of industrial processes, but it will be sufficient here just to enumerate a few of them: thus it has been used as a medium for paints (Johnson, Eng. Pat. 82, 1883), in the preparation of adhesive cements, as a precipitant of sewage in the alum, blood, and clay process, and in the manufacture of pure animal charcoal.

Tests for blood. It is often necessary, in medico-legal practice, to be able to identify blood-stains on garments and instruments. If the blood is fresh, a microscopic investigation reveals the presence of corpuscles, and an aqueous extract will show the typical absorption bands of hæmoglobin with the spectroscope. The best chemical test is the formation of hæmin crystals already described, and is given by quite small quantities of blood, even if it is old and dry. When the blood is dry, and small quantities only are present, the most delicate spectroscopic test consists in dissolving it in dilute potash with the aid of heat, and then adding a drop of a reducing agent such as ammonium sulphide; the two absorption bands of hæmochromogen are then seen, one about half-way between the D and E lines, and the other just on the blue side of the E line.

Human blood can only be distinguished with certainty from the blood of other animals by the so-called 'biological reaction.' The injection in successive doses of blood of another species into an animal acts as an antigen, and causes the development in the blood of the injected animal, of a specific 'precipitin'; the addition of the blood to the serum of the animal which furnished the injected blood causes a precipitate; and such a precipitate does not form except between the blood of the two species of animal used in the experiment. This has been applied to the case of human blood, by taking a rabbit and injecting human blood into it. The serum of this rabbit will then give a precipitate with the blood of man (and to a less extent of the higher apes), and with the blood of no other species of animal. The test is extraordinarily delicate, and will detect human blood that has been dried for months, and even when it is mixed with the blood of other animals. W. D. H.

BLOODSTONE. A popular name for the mineral heliotrope, a variety of chalcedony (SiO_2), showing bright-red spots on a dark-green ground. It is much used for the engraving of ring-stones and seals.

The same name has also been used for hæmatite (Fe_2O_3), being a translation of *αἱματίτης*, so called because the colour of the powdered mineral is like that of dried blood. L. J. S.

BLOOM. A term given to a mass of iron after it leaves the puddling furnace (*v.* IRON).

BLOOMERY. An old term for an iron furnace.

BLOWN OILS *v.* OILS and FATS.

BLOWPIPE *v.* ANALYSIS.

BLUBBER OILS *v.* OILS and FATS.

BLUE, ACETIN, *Coupier's blue* (*v.* INDULINES).

BLUE, ALIZARIN. This name is given to *dioxyanthraquinone-quinoline* $C_{17}H_9NO_4$, and its *sodium bisulphite compound*

$$C_{17}H_{11}NO_{10}S_2Na_2$$

(*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

BLUE, ALKALI, NICHOLSON'S BLUE or **SOLUBLE BLUE** *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, ANILINE. GENTIAN BLUE, OPAL BLUE, NIGHT BLUE, LIGHT BLUE, or **FINE BLUE** *v.* TRIPHENYLMETHANE COLOURING MATTERS; also ANILINE BLUE.

BLUE, ANTWERP, *v.* PIGMENTS.

BLUE, AZO-, *v.* AZO- COLOURING MATTERS.

BLUE, AZODIPHENYL, ACETIN BLUE, COUPIER'S BLUE, INDULIN, FAST BLUE R. $C_{18}H_{16}N_3Cl$ (*v.* INDULINES).

BLUE, BASLE. *Tolyldimethylaminophenotolyliminonaphthazonium chloride* $C_{32}H_{29}N_4Cl$ (*v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM).

BLUE, BAVARIAN, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, BENZIDINE, *v.* AZO- COLOURING MATTERS.

BLUE BLACK *v.* AZO- COLOURING MATTERS.

BLUE, BLACKLEY, *v.* INDULINES.

BLUE, BRILLIANT COTTON, METHYL BLUE, METHYL WATER BLUE. *Soda salt of triphenyl-β-rosanilinetrisulphonic acid* (*v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, CERULEAN, *v.* PIGMENTS.

BLUE, CHINA, WATER BLUE 6 B EXTRA, OPAL BLUE, COTTON BLUE, MARINE BLUE, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, CHINESE, or **PRUSSIAN BLUE** *v.* CYANIDES; also PIGMENTS.

BLUE, COBALT, *v.* COBALT; also PIGMENTS.

BLUE, COTTON, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, COUPIER'S, *v.* INDULINES.

BLUE, CYANINE, *v.* PIGMENTS.

BLUE, DIPHENYLAMINE, BLEU DIRECT *Triphenyl-β-rosaniline hydrochloride* (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

BLUE-ETHYLENE *v.* THIONINE COLOURING MATTERS.

BLUE, FAST, MELDOLA'S BLUE, NEW BLUE, NAPHTHYLENE BLUE. *Chloride of dimethylphenyl-ammonium-β-naphthoxazine* (*v.* OXAZINE COLOURING MATTERS).

BLUE, FLUORESCENT, *v.* BLEU FLUORESCENT.

BLUE, GENTIAN, SPIRIT BLUE O, OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE, FINE BLUE, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, INDIAN, *v.* PIGMENTS.

BLUE, INTENSE, *v.* PIGMENTS.

BLUE IRON-EARTH. An earthy blue variety of the mineral vivianite, a hydrated ferrous phosphate $Fe_3P_2O_8,8H_2O$, often found as a blue powder encrusting vegetable remains in bog-iron ore, peat, and clays. L. J. S.

BLUE, LEITCH'S, *v.* PIGMENTS.

BLUE, LIGHT, BLEU LUMIÈRE, LYONS BLUE, OPAL BLUE, BLEU DE NUIT *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, METHYLDIPHENYLAMINE

$$C_{39}H_{34}N_3Cl$$

obtained in 1874 by Girard by the action of oxalic acid upon methyldiphenylamine. Or by the action of copper nitrate (Bardy and Dusart). Or with chloranil (Geigy). No longer made.

BLUE, METHYLENE, *v.* THIONINE COLOURING MATTERS.

BLUE, NEUTRAL, *v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM.

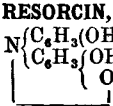
BLUE, NILE, *v.* OXAZINE COLOURING MATTERS.

BLUE, PARIS, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, PRUSSIAN, *v.* CYANIDES; also PIGMENTS.

BLUE, QUINOLINE, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE RED *v.* AZO- COLOURING MATTERS.

BLUE, RESORCIN, or **LACMOID** $C_{12}H_9NO_4$? probably  a colouring matter obtained by Weselsky and Benedikt in 1880, by the action of sodium nitrite on resorcin. Blue violet powder soluble in water. Soluble in alcohol with blue colour and dark-green fluorescence. Used as an indicator in alkalimetry (*q.v.*).

BLUE, SAXON, *v.* COBALT.

BLUE, VICTORIA, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE COPPERAS, BLUE STONE, or BLUE VITRIOL. *Copper sulphate* (*v.* COPPER).

BLUE GUM TREE. The *Eucalyptus globulus* (Labdll.), a tree common in Tasmania and South-Eastern Australia.

BLUE JOHN. A variety of fluor-spar found in Derbyshire, and valued for making ornamental articles (*v.* CALCIUM).

BLUE LEAD. A term applied to galena by miners to distinguish it from white-lead ore, or carbonate.

BLUE PIGMENTS *v.* PIGMENTS.

BOBBINITE *v.* EXPLOSIVES.

BODY VARNISH *v.* VARNISH.

BOFFINITE. An explosive consisting of potassium nitrate, 62–65 pts.; charcoal, 17–19½ pts.; sulphur, 1½–2½ pts., copper sulphate and ammonium sulphate, 13–17 pts.

BOG BUTTER. A substance resembling adipocere (*q.v.*), occasionally found in peat in Ireland and elsewhere. (For list of chemical and physical constants of a sample of bog-butter found in Tyrone, *v.* Radcliffe and Maddocks, J. Soc. Chem. Ind. 1907, 3.)

BOGHEAD COAL *v.* PARAFFIN.

BOGHEAD NAPHTHA *v.* PARAFFIN.

BOG-IRON-ORE. An impure iron hydroxide of recent formation in bogs and marshes. It is referable to the mineral species limonite ($2Fe_2O_3$, $3H_2O$), and, in fact, this name (from λειμών, a meadow) was at first applied to this material, which is known in German as Raseneisenstein or Wiesenerz (meadow-ore). It is sometimes placed under the species limnite (from λίμνη, a marsh), to which the formula $Fe_2O_3,3H_2O$ is assigned. It contains 20–78 p.c. Fe_2O_3, some silica and organic matter, and often phosphates in considerable amount. The material has been deposited by the oxidation, through the agency of algæ and bacteria, of chalybeate waters. It is dug in shallow pits in the peat-bogs of Ireland, the production amounting to a few thousand tons per annum, and is mainly used for the purification of coal-gas. The Swedish lake-ores (sjömalm) are of the same nature. L. J. S.

BOG MANGANESE, *wad*, or earthy manganese (*v.* MANGANESE).

BOHEMIAN BOLE. A yellow variety of bole (*q.v.*).

BOILED OIL. Linseed oil (*v.* LINSEED OIL).

BOILER INCRUSTATIONS AND DEPOSITS. The use of certain kinds of feed water in boilers leads to the formation of a deposit which, settling on the bottoms, tubes, and furnace crowns, hardens there and gives rise to an incrustation, which, by checking the transmission of heat to the water, causes waste of fuel and damage to the plates.

No such thing exists as an *absolutely* pure natural water, the nearest approach to it being rain water collected from a clean country watershed. Such water is the best natural kind that can be used in generating steam, its only drawback being that it exerts a solvent action upon metal fittings.

Temporary hardness.—Rain water in falling through the atmosphere dissolves only gaseous matter, which is again driven out on heating, and the collection of impurities by the water from an engineering point of view commences only when the rain comes in contact with the soil. The rain water falling on the ground penetrates the top and subsoil, which contain decaying vegetation, giving rise to carbon dioxide. The water, as it slowly filters through the soil, becomes saturated with the gas, and, bearing it in solution, penetrates the earth below. Here it meets with such substances as common salt (sodium chloride), compounds of magnesium, and calcium sulphate, small quantities of which the water dissolves partly by its own solvent powers, and partly by the agency of the dissolved carbonic acid. The chief substance dissolved by the aqueous solution of carbon dioxide is chalk or calcium carbonate, and to

a less extent the carbonates of magnesium and iron. These are converted into soluble bicarbonates, which readily dissolve in water, and endow the water with the property known as 'temporary hardness.'

The characteristics of hard water are too well known to need description. The hardness due to dissolved bicarbonate of lime is said to be temporary, because anything which will break up this salt and take away the carbon dioxide which enables it to remain in the soluble form, will throw down insoluble calcium carbonate rendering the water far softer. On boiling a hard water, the bicarbonate is decomposed, the hot water no longer holds the carbon dioxide in solution, and the calcium carbonate deposits and forms the 'fur' in the kitchen kettle or the far more serious boiler deposit, which is one of the greatest troubles with which the steam user has to contend, and which increases and thickens until at length a thorough clean out of the boiler has to take place.

Permanent hardness.—When the temporary hardness has been removed from water by boiling or other means, it is found that there is another kind of hardness which still remains, and this is called 'permanent hardness,' because it cannot be got rid of by those processes which serve to soften water rendered 'hard' by bicarbonate of lime. Permanent hardness in water is due to calcium sulphate (sulphate of lime or gypsum) and to the chloride and sulphate of magnesium, substances which are dissolved by the solvent power of the water itself, and these can be removed only by distillation or by the use of some chemical means, which will convert these soluble salts into insoluble bodies.

The hardness of a water is expressed in degrees, one degree of hardness representing the soap-destroying power imparted to one gallon of it by the presence in solution of one grain of chalk, so that a water is said to be of ten degrees of hardness when it contains 10 grains of chalk per gallon of water, or its equivalent in other lime and magnesium salts.

Formation of deposit.—The scale-forming constituents in natural waters are calcium bicarbonate, magnesium bicarbonate, calcium sulphate, and silica; whilst waters which contain sulphates, chlorides, and nitrates of magnesium also aid in the production of scale by decomposition amongst themselves. In tracing the formation of scale it will be well to consider the actions which lead to the deposition in the case of each ingredient.

Calcium carbonate, which is generally the most abundant constituent of fresh-water scale, is formed, as pointed out above, by the decomposition of soluble calcium bicarbonate with escape of carbon dioxide and deposition of practically insoluble calcium carbonate, whilst calcium sulphate, which is the most important factor in the hardening of scale, is deposited from water containing it by a totally different set of actions. Calcium sulphate is dissolved by the solvent power of the water itself, and not by the agency of carbon dioxide, and therefore the mere act of boiling water at ordinary pressures does not suffice to cause its deposition. The solubility of calcium sulphate varies very considerably with the temperature, as is shown by the following figures:—

100 parts of pure water at a temperature of F°.	C°.	Dissolve parts of calcium sulphate
32	0	0·205
41	5	0·219
53·6	12	0·233
68	20	0·241
86	30	0·249
95	35	0·254
104	40	0·252
122	50	0·251
140	60	0·248
158	70	0·244
176	80	0·239
194	80	0·231
212	100	0·217

It will be seen that calcium sulphate is most soluble in water at 95°F. (35°C.), one part of the salt being dissolved by approximately 400 parts of water; and inasmuch as the solubility of the salt is considerably decreased at 212°F. (100°C.), if a saturated solution at 35°C. be heated up to 100°C. precipitation of a portion of the calcium sulphate will take place, whilst at the temperature existing in high-pressure boilers, it becomes insoluble and is all precipitated.

The presence of magnesium hydroxide in boilers is generally ascribed to the mutual decomposition of the water and magnesium chloride, which give rise to magnesium hydroxide and hydrochloric acid, the action being accelerated by the presence of metallic iron, thus:

Magnesium chloride		Water		Magnesium hydroxide		Hydrochloric acid
$MgCl_2$	+	$2H_2O$	=	$Mg(HO)_2$	+	$2HCl$

When sea water is evaporated in contact with a large surface of metallic iron, no chloride can be detected in the distillate until four-fifths of the water has been distilled over, whilst if the sea water be evaporated out of contact with iron, it can be taken nearly to dryness without any decomposition. At the high temperature and pressure in marine boilers, the decomposition of magnesium chloride takes place; but a much larger proportion of the magnesium hydroxide is formed by the decomposition of the magnesium carbonate first deposited from the water in contact with the heated tubes, and also by the action of magnesium chloride in the sea water upon the deposited calcium carbonate, which react upon each other, forming soluble calcium chloride and magnesium hydroxide, which is precipitated, carbon dioxide at the same time escaping.

The substances referred to form the chief constituents of the boiler scale from whatever water it may be deposited, although traces of other bodies may be formed by local impurities in the water used. The chief differences in boiler scale are due to variations in the proportions of the calcium carbonate and sulphate.

Composition of fresh and salt waters.—Fresh water is very variable in composition, but its chief saline constituents are the carbonates of calcium and magnesium held in solution by carbon dioxide, together with the sulphates of these metals, and traces of common salt.

Although sea water is only river water concentrated by the evaporative power of the sun's rays during long ages, yet, owing to the deposition of calcium carbonate during the flow of the river and its utilisation by certain forms of marine life, the percentage of calcium carbonate

is reduced to a mere trace, whilst common salt has become the most important constituent. Calcium and magnesium sulphates, together with magnesium chloride, are also present in large quantities.

The following analyses will give an idea of the wide differences existing between fresh and salt water:—

SALTS IN SOLUTION IN RIVER AND SEA WATER: GRAINS PER GALLON.

	River water	Sea water
Calcium carbonate	10·80	3·9
Calcium sulphate	3·00	93·1
Magnesium sulphate	0·25	124·8
Magnesium chloride		220·5
Magnesium carbonate	1·25	trace
Silica	0·56	8·4
Sodium chloride	1·80	1850·1
Oxides of iron and alumina	0·27	trace
Organic matter	2·36	trace

When marine boilers were worked at comparatively low pressures, sea water was nearly always employed, but on the introduction of high-pressure tubular boilers, the quantity of deposit formed was so serious and the amount of labour required to remove the incrustation from between the tubes so considerable that it became imperative to discontinue the use of sea water, and to use distilled water for the boilers, condensing the steam after use and returning it to the boiler, and making up any loss with fresh water.

Distilled water is free from dissolved solids, but the condenser water always contains some of the lubricants from the engine cylinders. When animal and vegetable oils were used for lubricating, this condenser water, added to the usual boiler feed, caused a large amount of damage to the boiler plates, on account of the superheated steam decomposing the oils with liberation of fatty acids; but with the mineral oils employed for lubricating at the present day, this trouble is to a great extent obviated.

Nature of river and sea water deposits.—Owing to the great difference between river and sea water, variations are found in the nature of the deposits from them, as is shown by the following analyses of incrustations in boilers using river, brackish, and sea water respectively:—

	River	Brackish	Sea
Calcium carbonate	75·85	43·65	0·97
Calcium sulphate	3·68	34·78	85·53
Magnesium hydroxide	2·56	4·34	3·39
Sodium chloride	0·45	0·56	2·79
Silica	7·66	7·52	1·10
Oxides of iron and alumina	2·96	3·44	0·32
Organic matter	3·64	1·55	trace
Moisture	3·20	4·16	5·90
	100·00	100·00	100·00

These may be taken as typical deposits, and show that the incrustation from fresh water may be looked upon as impure calcium carbonate with small quantities of other compounds; that with a mixture of fresh and salt water, the deposit consists of nearly equal parts of calcium carbonate and sulphate, whilst sea water gives practically impure calcium sulphate.

The condition and physical properties of the deposit are largely affected by the presence of calcium sulphate, for that salt separates out in a fine needle-shaped crystalline form, which, aided by the magnesium hydroxide, binds the deposit into a hard mass. On the other hand, a deposit consisting of calcium carbonate without any sulphate forms a soft powder, which remains suspended in the water for some time, and which, as it settles in the form of a mud, admits of easy removal by the use of the sludge cock; but if calcium sulphate is present, the hardness of the scale is so great as to necessitate the use of a chisel and hammer to detach it from the plates and tubes, tending to injure the boiler and shorten its life.

On concentrating sea water, three stages of deposition may be traced:

1. Deposition of basic magnesium carbonate;
2. Deposition of calcium carbonate with remaining traces of the basic magnesium carbonate; and finally,
3. Deposition of the calcium sulphate.

The following table gives the variation in the saline constituents in the remaining liquid:—

Density	1·029	1·05	1·09	1·225
Sodium chloride	2·6521	4·4201	7·9563	23·8689
Calcium sulphate	0·1305	0·2175	0·3915	*nil*
Calcium carbonate	0·0103	0·0171	*nil*	*nil*
Magnesium carbonate	0·0065	0·0032	*nil*	*nil*
Magnesium chloride	0·2320	0·3865	0·6960	2·0880
Magnesium sulphate	0·1890	0·3150	0·5670	1·7610

If the sea water be concentrated above a density of 1·225, the sodium chloride commences to crystallise out.

Two causes affect the deposition of the calcium sulphate during the concentration of the sea water: first, although it is more soluble in a dilute solution of salt than in fresh water, it reaches its maximum solubility at a density of 1·033, and after this point concentration of the saline solution diminishes the amount held in solution. The calcium sulphate is insoluble in saturated brine. The second cause affecting the deposition is due to the density increasing as the temperature rises; the higher the temperature, the smaller is the amount of calcium sulphate which the water can hold in solution, so that when a temperature of 284°–302°F. (140°–150°C.) is attained, it becomes insoluble both in sea and fresh water.

Under ordinary conditions it is quite possible to boil sea water without the deposition of calcium sulphate, if care be taken that its density does not rise above 1·09, but in a boiler, pressure and consequent raising of the boiling-point come into play, and act upon the calcium sulphate in solution in exactly the same way as concentration and increased temperature, so that even in the old form of low-pressure boiler most of the sulphate was deposited, whilst in the high-pressure boilers now in use, every trace of the sulphate will be precipitated; and hence, owing to the impracticability of getting at the tubes in such boilers, it is impossible to use sea water in them, so that they require to be fed with fresh water. Even the fact of diluting the sea water with distilled water to reduce its density does not overcome this difficulty, so that when through a break-down in the distilling

plant, sea water has to be used, a slight scale is sure to be formed. When a saline solution containing calcium sulphate is heated under pressure or concentrated until calcium sulphate begins to deposit, the separation will continue even after the solution has cooled down or the pressure removed, and calcium sulphate when it has been deposited under pressure or high temperature from sea water, even if the density of the water is normal, redissolves only at a rate so extremely slow that it may be looked upon as practically insoluble.

This result is due to the mode in which the sulphate separates from sea water under pressure. Calcium sulphate occurs naturally as *gypsum* $CaSO_4,2H_2O$. When calcium sulphate is deposited from sea water in a boiler, it comes down in small crystals of the composition $2CaSO_4,H_2O$, whilst after deposition in the boiler and in contact with the heated plates and tubes, it loses all the water, changes its crystalline form to long needle-shaped crystals, and becomes *anhydrite* $CaSO_4$, and in this form it binds deposits into a hard mass.

Means of preventing incrustation.—The importance of getting rid of boiler deposits and of keeping the plates as clean as possible has led to innumerable methods being tried for the prevention and removal of incrustations.

With a very hard water or one containing ingredients which cause deposits in the boilers, it is impossible to do much good in the boiler itself, and the best way is to treat the water before it is put into the boiler by some such rapid method of precipitation and filtration as the Porter Clarke process, but for any such process to be effective, care must be taken not to overdo the softening by adding too much of the precipitants, as an excess of calcium hydroxide in the water gives rise to as much trouble in the boilers as if the ordinary lime salts had been present.

It is quite possible to so treat even sea water as to make it available for boilers, and experiment has shown that, using sea water so treated, a boiler which had been kept steaming continuously for a month, when opened, was found to be in perfect working order, but in this case also the sea water cannot be treated in the boilers themselves, otherwise very heavy deposits would be formed.

In fresh-water boilers incrustation can to a certain extent be prevented, or at any rate diminished, by the addition of substances which will prevent the calcium sulphate binding the calcium carbonate into a hard mass, and these so-called anti-incrustators may be divided into two classes :

1. Those which have some definite chemical action.
2. Those which are purely mechanical in their action.

In saline anti-incrustators sodium carbonate in one form or another generally plays the principal part. Its action is to convert the calcium sulphate and magnesium chloride into carbonate, and at the same time to keep the water in an alkaline condition so as to prevent any damage from acids.

Calcium sulphate		Sodium carbonate		Calcium carbonate		Sodium sulphate
$CaSO_4$	+	Na_2CO_3	=	$CaCO_3$	=	Na_2SO_4

With the removal of the calcium sulphate the calcium carbonate is precipitated in a soft and powdery condition, and is easily blown-off by the sludge cock.

Other alkalis and alkaline salts are also employed, amongst which may be mentioned ammonium chloride, which decomposes the calcium carbonate in the boiler, forming soluble calcium chloride, whilst the ammonium carbonate volatilises with the steam.

Although acid mixtures have been recommended, yet it is evident that, even if they are effective in removing the scale, they must have a detrimental effect on the boiler plates.

Feed-water heaters act to a certain extent in softening the water supplied to a boiler, and thus aid in reducing incrustation ; as much as 50 p.c. of the calcium carbonate in the water will often be found deposited as mud in the superheater.

In the anti-incrustators which have merely a mechanical action, some act by offering surfaces on which the deposits will form in preference to depositing on the plates, as in the case of fibre brushes or bundles suspended in the boiler, and which can be easily withdrawn ; whilst the bulk of them consist of finely divided organic matter of an insoluble character, which, by settling with the deposit, prevents the crystallisation of the calcium sulphate binding the mass into a hard crust, and so allows the sludge cock to get rid of the loose deposit. Spent tan is a good example of this class of anti-incrustator as not only does it prevent binding of the deposit, but it also blackens any scale that exists by the formation of tannate of iron, so making the boiler look clean.

Deposits caused by lubricants entering boiler.—As before mentioned, many of the inconveniences arising from the use of animal and vegetable oils can be avoided by the employment of mineral oils as lubricants, but with the introduction of high-pressure steam even mineral lubricants used in the cylinders have become a source of trouble, as, when used too freely or when they are not of good quality, they may give rise to a dangerous form of deposit, and with high-speed engines give a great amount of trouble in the boilers.

In 1878 the furnaces of the s.s. *Ban Righ* and the screw tug *Ich Dien* collapsed without apparent reason. The only clue to the cause was a certain amount of oily deposit which had formed on the tops of the furnaces, and the result of experiments made by Mr. Dunlop, of Port Glasgow, showed that this oil, which had found its way into the boiler from the cylinders, was so bad a conductor of heat that its formation on the plates allowed them to get overheated ; they were thus unable to withstand the pressure of steam in the boiler, and collapsed.

Instances of collapse from similar causes became increasingly frequent, no less than thirty occurring within a few years. The causes which occasioned them were not at first sight apparent ; the scale upon the furnace tops where the collapse had taken place was not only free from oil, but perfectly harmless both in quantity and quality. On closer investigation, it was evident that this scale was not in the condition in which it was formed originally, as the deposits from the bottom of the boiler tubes, from the bottom of the furnaces and from the shell of

the boiler, were rich in oily matter, and it was impossible that the furnace tops could have escaped being coated during this deposition. Experiment soon pointed out the reason for this anomaly, and revealed the actions which had taken place.

In a case which was thoroughly investigated, the pressure at which the boilers were worked was 80 lbs. per square inch, corresponding to a temperature of 311°F. (111°C.), which was so far below the boiling-point of the lubricant that it was evident that it had not distilled in the usual way. Experiment showed that the fact that a lubricant had a higher boiling-point than the temperature of the steam, is no guarantee that no oil will enter the boiler, as under the influence of steam, heat, and pressure the hydrocarbons of high boiling-point break up into simpler ones boiling at lower temperatures. Having thus found its way into the boiler, the particles of oil coalesce and form a scum on the surface of the water, with no tendency to sink, since the specific gravity is about 0·889. Small particles of calcium sulphate, which is nearly always present owing to small leakages of sea water in the condensers, adhere to this scum, and, becoming coated with oil, stick to one another and to any surface with which they come in contact. The particles thus coated with oil have the same specific gravity as the water, and rise and fall with the convection currents, sticking to any surface against which they strike, and in this way depositing themselves, not, as in common incrustations, on the upper surfaces, but also on the under sides of the tubes. The deposit so formed is a bad conductor of heat, and its oily nature tends to prevent intimate contact between the water and itself. When this occurs on the crown of the furnaces, overheating of the plates is the consequence, and the deposit begins to decompose by heat, the lower layer next the plates giving off gases which blow up the greasy layer and render it porous, thus making it a still worse conductor of heat. The plate then becomes heated to redness, and being unable to withstand the pressure of steam, collapses. During the last stages of the overheating the oily matter has decomposed thoroughly and burns away, or rather is distilled off, leaving behind, as an apparently harmless deposit, the solid particles round which it had originally formed.

This oily deposit will more likely be produced with fresh or distilled water, owing to the low density enabling the deposit to settle more quickly; it is evident also that when this oily scum has been formed in the boiler it is dangerous to blow off without first using the scum cocks, as, whilst the water is sinking, the scum clings to the surfaces of the furnaces, &c., and on filling with fresh water, remains there, causing rapid collapse. A remarkable instance of this occurred in the case of a large vessel in the Eastern trade, in the boilers of which an oily scum had formed. The ship stopped at Gibraltar, and the engineer blew out his boilers, filling up with fresh water, with the result that before the ship had been at sea ten days most of the furnaces had come down.

Under some conditions the oily scum coagulates with the solid particles into a thin cake, which sinks and forms a patch on the crown of the furnaces at one spot, the result being the formation of a 'pocket' by the local bulging of the plate.

In these oily deposits copper is sometimes found in considerable quantity, due to the slight solvent action of the mineral oils upon copper and its alloys, used in the fittings of the cylinders and condenser.

Experiments with such deposits have shown that even if they are only one-sixteenth of an inch in thickness, the furnace crown can be heated to redness, whilst with an oxy-hydrogen flame the metal can be burnt through in a thin wrought-iron plate.

Experiments upon the power of plates to transmit heat bring out the effect of oily deposits in an extraordinary way, as it has been shown that merely wiping the surface of a plate with a greasy rag hinders the transmission of heat to a very considerable extent, and that a thin film of oil is as prejudicial as a couple of inches of boiler scale.

In connection with the question of deposits caused by lubricants entering the boiler, it may be stated that the chief essentials of a good lubricating oil are that it shall be a pure mineral oil, and that its distilling point in steam shall be higher than that of the steam in the cylinder. Such oils can be readily obtained, but as the process of extracting the low boiling-point oils is expensive, their price is necessarily high. Any lubricant which requires animal or vegetable oils to give it body should be rejected.

Mineral oils are not fats, but hydrocarbons—compounds of carbon and hydrogen—differing widely from animal and vegetable oils, which are liable to be decomposed with liberation of fatty acids. The fatty acids are set free by the action of high-pressure steam, and attack iron, copper, and copper alloys with great readiness, forming metallic soaps, and thus cause serious damage to both boilers and fittings. Another objection to animal and vegetable oils is their tendency to oxidise, forming a gummy resinous substance.

The prevention of oily deposits.—The general methods adopted to prevent the condenser water introducing oily matter to the boiler are:

1. Cleansing the steam in an exhaust steam separator.
2. Passing the condenser water through a feed-water filter.

The great advantage of the former method is that most of the oily matter is abstracted before the condensers are reached, and greasing of the condenser tubes is prevented, and as the action of the grease is to prevent proper contact between the water and the metal surface, the loss of condensing power due to a small quantity of oil is very great, and may cause a loss of from 8 to 15 p.c. in efficiency after a few hours' steaming.

In these exhaust steam separators the rate of flow of the steam is reduced by leading it into an enlarged chamber, and causing it to impinge on surfaces to which the oily particles adhere. There are several types made, and the results are satisfactory, but they do not always ensure freedom from traces of oil.

Feed-water filters may be either mechanical scrubbers, in which coke, charcoal, sawdust, crushed quartz, or other inert material exposing

a large surface, may be used, or they may be surface filters, in which the water passes through cloths fixed on frames, and these filters may be fixed between the feed pump and boiler, in which case they are under heavy pressure; or they may be used as gravity filters before the feed pump is reached, in which case filtration is carried on more slowly and the separation is far more satisfactory, the drawback, however, being that they occupy more space. It has been found that to ensure complete separation of the oily particles, it is highly advantageous to add small quantities of aluminium sulphate to the condenser water in a treatment tank before filtration, as this causes coagulation of the fine particles of oil emulsified in the water, and leads to their easy separation in the filter. V. B. L.

BOIS-PIQUANT BARK. The bark of *Zanthoxylum caribæum* (Lam.), and *Z. Perrottetii* (D.C.). Used in France as a febrifuge (Heckel a. Schlagdenhaffen, Compt. rend. 98, 996).

BOLDO. A shrub, *Peumus boldus* (Molina), belonging to the *Monimiaceæ*, growing in the Chilian Andes. The bark is used in tanning, the wood makes a good charcoal, and the bark and leaves contain a glucoside $C_{30}H_{52}O_8$, useful as a hypnotic and cholagogue (Chapoteau, Compt. rend. 98, 1052).

BOLE. (*Bol*, Ger.) A ferruginous clay-like substance, of red, brown, or yellowish colour. It is not plastic, and when thrown into water falls to pieces with emission of streams of minute air-bubbles. It has an unctuous feel, and some varieties adhere to the tongue. When cut it presents a shining streak. Before the blowpipe it fuses to a yellowish or white enamel. Its composition is very variable, but its usual limits are from 41 to 47 p.c. SiO_2, 18 to 25 p.c. Al_2O_3, and 24 to 25 p.c. H_2O, with a proportion of Fe_2O_3 which may reach 12 p.c. It will be noticed that the percentage of water is higher than in clays. The *Fettbol* of Freiberg in Saxony occurs in mineral veins, and contains only about 3 p.c. of Al_2O_3. The bole of Stolpen in Saxony is a yellowish substance containing only a trace of Fe_2O_3. Rammelsberg's analysis yielded SiO_2, 45·92; Al_2O_3, 22·14; CaO, 3·9; H_2O, 25·86. In the 'bole of Sinope' (sinopite) from Asia Minor the SiO_2 falls as low as 32 p.c. The ancients obtained this material from Cappadocia, and used it as a red pigment. It was also employed in medicine as an astringent (*v.* LEMNIAN EARTH).

The following is an analysis of bole, occurring in granite, at Steinkirchen, Bohemia:—Dried at 100° it yielded SiO_2, 46·73; Al_2O_3, 26·17; Fe_2O_3, 12·34; CaO, 1·64; MgO, 1·31; K_2O, 0·98; MnO, 0·28; loss on ignition, 10·53 (G. Starkl, Verh. k. k. Geolog. Reichs. Vienna, 1880, 279).

Bole is frequently found as a product of the decomposition of basaltic rocks. Thus the sheets of basalt in N.E. Ireland, representing Tertiary lava-flows, are separated by partings of bole, associated with lithomarge, bauxite, pisolitic iron-ore, and seams of lignite. The Antrim bole is described as a poor variety of aluminous iron-ore (Tate and Holden, Quart. Jour. Geol. Soc. 26, 1870, 155; G. H. Kinahan, Jour. R. Geol. Soc. Ireland, 16, 1886, 306; P. Argall, *ibid.* 98). L. J. S.

BOLOGNIAN PHOSPHORUS *v.* BARIUM.

BOLOGNIAN STONE. A native variety of barium sulphate found as nodular masses embedded in clay near Bologna; when partially reduced to sulphide by calcination with charcoal, it exhibits phosphorescence (*v.* BARIUM).

BOLORETIN *v.* RESINS.

BOMBICESTOROL *v.* STEROLS.

BONE. Bony tissue may be either compact as in the shafts of the long bones, or spongy or cancellated as in the flat bones of the skull and in the extremities of the long bones; here an external compact layer encloses a mass of spongy bone or diploë. From the embryological point of view, bones may be divided into cartilage bones and membrane bones. The cartilage bones are those which in embryonic life are preceded by cartilaginous prefigurements; these comprise the majority of the bones in the body, and include all the long bones except the clavicle. In the case of membrane bones (for instance, the flat bones of the cranium), there is no such preliminary cartilaginous prefigurement. It must not, however, be supposed that in the cartilage bones the cartilage is converted into bone; for here, as in the cases where there is no cartilage present, the true bony tissue is laid down by the agency of certain cells termed osteoblasts in the connective tissue sheath (periosteum) of the bone, and the cartilage when present, after undergoing a certain amount of calcification, is then entirely eaten away by certain large cells called osteoclasts. In the cartilaginous, as distinguished from the bony or teleostean, fishes, the replacement of the cartilage by true bone does not occur.

Bone is deposited in concentric laminæ, the majority of the layers encircling the channels called Haversian canals, in which the blood-vessels lie. The living elements in bone, the bone cells, lie in spaces between the laminæ, and these spaces (lacunæ) intercommunicate by minute canals, in which lymph flows and maintains their nutrition.

The chemical materials present are organic and inorganic. The organic materials are proteins and nucleïn derived from the bone cells, a small quantity of an elastin-like substance which forms a lining to the Haversian canals, and a mucoid or glucoprotein; but the principal organic material, sometimes misnamed bone cartilage, is better termed ossein. Ossein is identical with the collagen of connective tissues, and like it yields gelatin on boiling with water. If the inorganic salts are dissolved out by mineral acids, the ossein remains as an elastic mass which preserves the original shape of the bone.

The inorganic constituents remain as the so-called bone earth after the bone is completely calcined; it consists chiefly of calcium phosphate, but also contains calcium carbonate, and small amounts of magnesium, chlorine, and fluorine. Gabriel (Zeitsch. physiol. Chem. 18) states that potassium and sodium also occur. Traces of iron come from the blood in the bone, and of sulphate from chondroitin-sulphuric acid (Mörner, *ibid.* 23).

Investigators differ as to the manner in which the inorganic substances are combined. Chlorine and fluorine are present in the same form as in apatite ($CaFl_2 \cdot 3Ca_3P_2O_8$), and according to Gabriel, the remaining mineral

constituents form the combination $3(Ca_3P_2O_8)$ $CaCO_3$. He gives as the simplest expression for the composition of the ash of bones and teeth the formula $Ca_3(PO_4)_2+Ca_5HP_3O_{13}+H_2O$, in which 2–3 p.c. of the lime is replaced by magnesia, potash, and soda, and 4–6 p.c. of the phosphoric acid by carbon dioxide, chlorine, and fluorine.

Zalesky's analyses (Hoppe-Seyler's Med. Chem. Untersuch. 19) show how closely bone earth agrees in composition in different animals. The figures represent parts per 1000.

—	Man	Ox	Tortoise	Guinea-pig
Calcium phosphate $Ca_3(PO_4)_2$ . .	838·9	860·9	859·8	873·8
Magnesium phosphate $Mg_3(PO_4)_2$ . .	10·4	10·2	13·6	10·5
Ca combined with CO_2, Fl, and Cl .	76·5	73·6	63·2	70·3
CO_2 (partly lost on calcining) . .	57·3	62·0	52·7	—
Chlorine . . .	1·8	2·0	—	1·3
Fluorine . . .	2·3	3·0	2·0	—

The various bones of the skeleton differ a good deal in the proportion of water, organic solids, and inorganic solids which they contain. This depends to some extent on the admixture of marrow, blood-vessels, and other formations from which it is difficult to entirely free the osseous tissue proper. The quantity of water in fresh bones thus varies from 14 to 44 p.c., and of fat between 1 and 27 p.c. The quantity of total organic substance varies from 30 to 52 p.c., the remainder being inorganic.

The marrow is from the chemical point of view mainly fat; its cells yield protein and nucleoprotein.

On a rough average it may be said that two-thirds of the solids consist of inorganic and one-third of organic compounds.

With regard to the minute composition of bones at different ages, we have no very accurate information. Voit found in dogs and Brubacher in children, that the water in the skeleton decreases and the ash increases with advance of years. Graffenberger's observations on rabbits confirmed this view.

A great many experiments have been made to determine the influence of food—for instance, rich or poor in lime salts—on the composition of bone, but the results have been doubtful or contradictory. The attempts to substitute other alkaline earths for lime have also given uncertain results (*see* H. Weiske, Zeit. f. Biol. 31; also Hammarsten's Physiol. Chem. translated by Mandel).

A large number of data have also been published regarding the variations in chemical composition in different diseases of bone. Thus in exostoses the inorganic material is usually increased; in rickets and osteomalacia, the proportion of water and osseïn to bone earth is raised. The view that lactic acid is responsible for the washing out of lime salts from bones in rickets is, however, usually discredited.

The somewhat rare condition of a curious protein (called Bence-Jones protein, after its discoverer) in the urine is almost invariably associated with bone disease (osteomalacia, or malignant new growths). This protein in many of its characters resembles a proteose, but is probably derived from the mucoid of osseous tissue (Rosenbloom, J. Biol. Chem. 1910, 7, 14; Williams, Bio. Chem. J. 1910, 5, 225).

On heating out of contact with air, bone evolves a large quantity of volatile matter (*v.* BONE OIL) which contains ammonia, pyridine bases, pyrrol, nitriles, &c. A black residue is left, consisting of the bone ash in association with carbon, which is called animal charcoal (*q.v.*).

The industrial uses of bone are very numerous and involve a large import trade; not only is the bone itself made into many utensils, but the materials made from the bone (charcoal, bone ash, gelatin, &c.) are put to many uses.

Thus animal charcoal or bone black is employed in many chemical operations, in sugar refining, as a polish for silver work, &c.

Bone meal and bone ash are extensively employed as manure, and in the preparation of the superphosphates of commerce.

The gelatin in an impure form is used in the preparation of paper, silk, furs, &c., and the purer varieties are also put to numerous uses, for instance, as a clarifying agent in the preparation of wines, beers, liqueurs, for food in the preparation of soups, jellies, and puddings, in the making of photographic films, and in Bacteriology for the preparation of culture media. (*See* Merck's Waren-Lexikon, arts. 'Knochen,' 'Knochenasche,' 'Knochenkohle,' 'Knochenöl'; H. Ost, Lehrbuch der Chem. Technologie, 6th ed. 1907, 'Knochenmehl,' 187, 'Knochenleim,' 621; Dammer, Handbuch d. chem. Technologie, 1898, 5, art. 'Knochenverarbeitung,' 254.)

The mention of gelatin as food suggests a word on its nutritive value. It is easily digestible and assimilable, and so is much employed in invalid cookery; nevertheless, it has long been recognised that it is of inferior nutritive value. If animals receive gelatin as their sole nitrogenous food, they waste and die more rapidly than if nitrogenous food is entirely withheld from them; still, when mixed with other proteins, less of the latter is sufficient to maintain life. Recent investigations on the chemistry of proteins have shown that gelatin is destitute of the tyrosine and tryptophane groups, and these groups appear to be of special value or even indispensable for tissue repair; the previously puzzling behaviour of gelatin in nutrition is thus explicable. W. D. H.

BONE ASH *v.* BONE and FERTILISERS.

BONE BLACK *v.* ANIMAL CHARCOAL.

BONE EARTH. The calcined residue of bones, consisting chiefly of calcium phosphate (*v.* BONE).

BONE FAT is the fatty matter contained in the bones of animals, and is practically a by-product in the process of working up bones, whether it be for the manufacture of bone char or for the production of glue and gelatin. In either of these manufactures, the 'degreasing' of the bones precedes all further manipulations. Bones from head, ribs, shoulder blades, &c., contain from 12 to 13 p.c. of fat, whilst the 'marrow' bones, *i.e.* the large thigh bones, contain as much as 18–20 p.c. Formerly bone fat was produced by boiling the broken bones with water in open vessels, and allowing the hot liquor to stand, so that the fat could separate

on the top and be skimmed off. In the case of fresh bones, the recovered bone fat had a white to yellowish colour, a faint odour and taste, and the consistence of butter. When putrid bones were employed, the bone fat passed, according to age and state of decomposition of the organic matter in the bones, through all gradations from a white fat to a dark rancid fat of a very disagreeable smell. The boiling-out process allows only about one-half of the fat to be recovered. The small yield, and the nuisance connected with the preparation of the bone fat forced the manufacturers to treat the bones with steam under pressure. The broken bones were placed in a cage fixed inside an autoclave, and were heated therein with open steam, under a pressure of 2 to 3 atmospheres. The bone fat so obtained was of the same quality as that prepared by the former process. The best bone fat obtainable in the market is at present prepared by this process, especially in the large packing houses of the United States and South America, where the bones are worked up in the fresh state. They are first washed in 'bone-washing machines.' These are cylinders usually 10 feet long and 3 feet to 4 feet in diameter, built up from iron bars, 1 inch apart, fixed into two cast-iron heads. They are driven by chain and sprocket, and rotate slowly, making about ten revolutions per minute. Through the entire length of the drum there is a hinged door made of bars, which allows the filling and emptying of the cylinder. The machines are usually set at an angle to facilitate the washing and emptying operations. Some manufacturers even resort to steeping the bones in a solution of sulphurous acid in order to obtain a whiter fat (as also a better glue) than unbleached bones afford. The yield of bone fat in the steaming-out process under pressure is considerably higher (by about 50 p.c.) than in the boiling-out process in open vessels, so that from bones containing 12 p.c. of fat, 8 to 9 p.c. can be recovered.

Bone fats of this quality can be bleached, but only the best kinds are likely to yield a good product. The higher the percentage of free fatty acids, the greater is the difficulty in bleaching. In fact, products containing more that 50 p.c. of free fatty acids could hitherto not be bleached successfully.

The highest yield of bone fat is obtained by treating the bones with an organic solvent, whereby the animal tissue remains unimpaired, so that the whole of the glue-yielding organic substances can be converted into glue after the fat has been removed. The solvent used in bone-extracting works is almost exclusively petroleum ether or Scotch shale oil, boiling between 100° and 130°. Proposals have been made to use carbon tetrachloride or chloro- compounds of ethylene and ethane. Experiments with carbon tetrachloride have, however, been abandoned as unremunerative. Extraction with 'benzin' or shale oil takes place in iron digesters under pressure or in open apparatus. The fat obtained by the extracting process is dark-brown, and has a very penetrating, unpleasant smell. In addition to a considerable amount of free fatty acids, it contains lime-soap, calcium lactate, calcium butyrate, and hydrocarbons from the 'benzin' which cannot be fully removed even by prolonged steaming. Hitherto, this kind of fat has not been treated successfully, and even when some immediate improvement was obtained, the colour and also the unpleasant smell 'reverted' after a short time. A patent by Volland (D. R. P. 222669) claims, however, to bleach extracted bone fat by means of barium peroxide.

The bone fat obtained by the boiling-out or steaming-out process can be used for soap making; the fat obtained by the extracting process is utterly unsuitable for that purpose in this country, on account of its rank smell. On the continent, however, such benzin-extracted fat is used up for soap in small quantities, especially when the price of fatty materials is high. The bulk of bone fat is, however, used in candle works, where it is hydrolysed in an autoclave and subsequently subjected to the usual acidifying and distilling processes.

Bone fat is an important article of commerce The chemical composition of bone fat lies midway between that of marrow fat and tallow. On account of the large amount of fatty acid contained in bone fat, this fat must be examined by special methods, for which the reader is referred to Lewkowitsch, Chemical Technology and Analysis of Oils, &c., ii. 623.

Bone oil, fatty bone oil (not to be confounded with Dippel's oil), is the liquid portion of bone fat which is sometimes prepared in the same manner as tallow oil is obtained from tallow. Bone oil is used as a lubricant, and in the leather industries replaces neat's foot oil in the preparation of 'fat liquor' and other emulsions. If such bone oil is free from fatty acids, it represents one of the best lubricating oils on account of its very low 'cold test.'

J. L.

BONE MEAL *v.* FERTILISERS.

BONE OIL. *Animal oil*; *Dippel's oil*; *Oil of hartshorn*; *Oleum animale empyreumaticum*; *Oleum cornu cervi*; *Oleum Dippelii.* (*Knochenol, Thierol,* Ger.) The product obtained by distilling bones in the preparation of bone black or animal charcoal.

The bones are first boiled in a large quantity of water, which removes the greater part of the fatty matters; they are then roughly dried and are subjected to dry distillation in iron retorts, similar to those used in the manufacture of coal gas. Bone black or animal charcoal remains behind and bone oil distils. The products of distillation are conducted through long iron tubes, which act as condensers and lead into receivers, where the crude bone oil collects, together with water. The gases are then passed into a separator containing sulphuric acid to retain ammonia, and can afterwards be used for heating purposes, or, if passed through purifiers, for illumination. The crude oil is separated from the aqueous distillate and is subjected to redistillation. The aqueous liquid consists of a solution of ammonium sulphide, ammonium thiocyanate and cyanide, ammonium carbonate, and small quantities of very volatile organic bases. This is treated with sulphuric acid and afterwards distilled with slaked lime. The distillate, on treating with solid potash, yields large quantities of ammonia, whilst some oily bases separate out, and are afterwards worked up with the bases contained in the crude oil. This latter is a

dark-brown, nearly black liquid, having a fœtid, most offensive smell, and a sp.gr. 0·970.

On subjecting it to redistillation it begins to boil at 80°, when quantities of ammonia come over together with an oil. The temperature rises very gradually to about 250°. From 180° upwards large quantities of ammonium cyanide and ammonium carbonate sublime over, and care has to be taken to prevent the condenser being stopped up. A black resinous tar remains, which is employed in making Brunswick black.

The following substances have been isolated from bone oil by fractional distillation combined with treatment with acids to separate basic from non-basic constituents :—

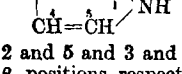
Chief constituents	*Subsidiary constituents*
Butyro-nitrile	Methylamine
Valero-nitrile	Ethylamine
Hexo-nitrile	Aniline
Isohexo-nitrile	Pyridine
Deco-nitrile	Methyl-pyridine
Palmito-nitrile	Dimethyl-pyridine
Stearo-nitrile	Quinoline
Pyrrol	Phenol
Methyl-pyrrol	Propionitrile
Dimethyl-pyrrol	Valeramide
Hydrocarbons C_9H_{14}	Toluene
Hydrocarbons $C_{10}H_{16}$	Ethyl-benzene
Hydrocarbons $C_{11}H_{18}$	Naphthalene

(Weidel and Ciamician, Ber. 13, 65).

As to the formation of the various compounds in bone oil, the nitriles are formed by the action of ammonia on the fatty acids, pyrrol and the pyrrols are the products of decomposition of the gelatinous substances, and pyridine and its derivatives are condensation products of acroleïn, from the dry distillation of the fats, with ammonia, methylamine, &c.

Pyrrol. That portion of the non-basic part of bone oil boiling at 98°–150° contains pyrrol and its homologues. That above 150° contains dimethylpyrrol. The fraction 140°–150° consists of a mixture of homopyrrols—*i.e.* methylpyrrols. To separate the α- and β- derivatives, the mixture is converted into the potassium compound by fusion with potash, and heated in a current of carbon dioxide to 200°. Two isomeric homopyrrol carboxylic acids are formed, which differ in the solubility of their lead salts. α-Homopyrrol carboxylic acid melts at 169·5°, and its lead salt is very soluble in water, differing from the β-acid, which melts at 142·1°, and forms a slightly soluble lead salt. The acids obtained respectively yield on distillation with lime the corresponding methylpyrrols. α-Homopyrrol boils at 148° under 750 mm. pressure, and β-homopyrrol at 143° at 743 mm.

The constitution of pyrrol is represented as follows :—



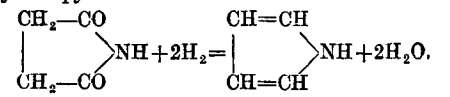
the positions 2 and 5 and 3 and 4 being known as the α- and β- positions respectively. It boils at 130°–131°, and its sp.gr. is 0·9752 at 12°. Refractive index $\mu_D = 1{\cdot}5074$ (Gladstone, Chem. Soc. Trans. 1884, 246). It is slightly soluble in water, readily soluble in alcohol and ether. It is a weak base, and is only slowly dissolved by dilute acids in the cold.

By the action of iodine on potassium pyrrol, tetriodopyrrol is formed, which crystallises in yellowish-brown prisms and decomposes at about 140°. It acts like iodoform as an antiseptic, and is known as iodol. It has the advantage over iodoform of being free from smell.

Pyrrol has been synthesised by passing acetylene and ammonia through red-hot tubes :

$$2C_2H_2 + NH_3 = C_4H_4NH + H_2 ;$$

also by distilling the ammonium salts of mucic and saccharic acids. Succinimide, on heating with zinc-dust containing zinc hydrate, also yields pyrrol



Potassium dissolves in pyrrol with the formation of potassium pyrrol C_4H_4NK, a substance insoluble in ether and decomposed by water into pyrrol and potassium hydroxide. This substance reacts with alkali iodides to form substituted pyrrols ; *e.g.* :

N-Methylpyrrol, $C_4H_4N{\cdot}CH_3$: boils at 113° ; sp.gr. 0·9203.

N-Ethylpyrrol $C_4H_4N{\cdot}C_2H_5$: boils at 131° ; sp.gr. 0·9042.

N-Phenylpyrrol $C_4H_4N{\cdot}C_6H_5$, obtained by distilling the anilides of mucic and saccharic acids, melts at 62°. The homologues of pyrrol contained in bone oil are, however, all substituted in the group C_4H_4.

By the action of benzalchloride on pyrrol in presence of sodium a phenylpyridine is obtained in which the phenyl is in the meta- position to the nitrogen (Ciamician and Silber, Ber. 20, 191).

By reducing pyrrol with zinc and acetic acid Δ^3 pyroline is produced (Ber. 1901, 3952). Electrolytic reduction to the same substance may be effected by suspending pyrrol in dilute sulphuric acid in the cathode cell of an electrolytic apparatus, the cathode being lead, and passing a current of density 1 amp. per sq. cm. Homologues may be similarly reduced (D. R. P. 127086, 1902).

Nascent hydrogen converts pyrrol into pyroline C_4H_6NH, a liquid boiling at 91° which dissolves easily in water. It yields, with nitrous acid, a nitrosoamine $C_4H_6N{\cdot}NO$, m.p. 37°, and on heating with methyl iodide gives methylpyrroline (Ber. 16, 1536).

Pyrrol is readily oxidised to *maleimide* $C_4H_3O_2N$, which forms faintly yellow crystals, melting at 93°, and readily yields a *dibromide*, melting at 226° under the influence of light and bromine water (Atti. R. 1904, (v.) i. 489).

The action of *formaldehyde* and *methylene chloride* on pyrrol is described by Pictet and Rilliet (Ber. 1907, 1166).

By the action of *chloroform* in absolute ether on the potassium derivative of pyrrol, chloropyridine is obtained.

Pyrrol derivatives condense with aldehydes under the following conditions : (1) When the derivatives contain at least one hydrogen atom combined with a carbon atom of the nucleus, either in the α- or β- position ; (2) when both α- and β- positions are occupied by substituents, no combination occurs even if the iminic hydrogen is present ; (3) pyrrol derivatives containing

more than one CH group in the ring may combine with aldehydes in molecular proportions (Ber. 1902, 1647).

Indole $C_6H_4\langle^{CH=}_{NH}\rangle CH$ is obtained by dissolving pyrrol in 10 p.c. sulphuric acid, allowing the mixture to stand 1–2 hours, and then distilling in steam after adding excess of sodium hydroxide. Diethyl indole prepared by this process is a viscid ill-smelling oil, boiling at 270°–310° (D. R. P. 125489).

Pyrrol may also be converted into indole by dissolving in dilute hydrochloric acid, adding slight excess of ammonia, filtering, extracting the filtrate twice with ether, and heating the tripyrroline obtained in the extract to above 300°, when indole and pyrrol result (Ber. 1894, 476).

Pyrrol may be converted into *tetramethylene diamine* as follows. On treatment with hydroxylamine, a solid compound, probably the dioxime of succinaldehyde, is formed, and this, by reduction with sodium and absolute alcohol, yields tetramethylene diamine.

Pyrrol derivatives of the constitution

$$\begin{array}{l} EtO_2C\cdot C{=}CMe \\ \quad\quad\quad\

By heating a mixture of glycerol and ammonium phosphate, a mixture of a large number of pyridine bases is formed. β-methyl, β-ethyl, probably β-propyl, pyridine, besides pyridine itself and homologues of the diazine $C_4H_4N_2$, have been recognised (Stoehr. J. pr. Chem. 1892, 20).

Pyridine is a liquid with a pungent smell, miscible with water; sp.gr. 0·9855 at 15°, and 0·9944 at 4°; and boils at 115·2°/760 mm. It forms a hydrochloride C_5H_5N,HCl, and a platinichloride $(C_5H_5NHCl)_2PtCl_4$. Sodium amalgam yields **piperidine**, *i.e.* hexahydropyridine, which is reconverted into pyridine on oxidation. It forms an ammonium iodide with alkyl iodides, and with chloracetic acid a pyridine-betaïne $C_5H_5N<^{CH_2}_{O}>CO$. By the action of sodium on pyridine a **dipyridine** $C_{10}H_{10}N_2$ is obtained, an oil boiling at 280°–281°/744 mm., which on oxidation with permanganate yields *iso*nicotinic acid. Together with dipyridine, a body *p*-dipyridyl is formed $NC_5H_4{\cdot}C_5H_4N$, which melts at 114° and distils at 304°. It also yields *iso*nicotinic acid on oxidation, and on reduction with tin and hydrochloric acid forms *iso*nicotine, which melts at 78° (Ber. 16, 423).

The isomeric *m-dipyridyl* is obtained from *m*-dipyridyldicarboxylic acid (by oxidising phenanthroline). It boils at 293°, and yields on reduction with tin and hydrochloric acid *nicotidine* $C_{10}H_{14}N_2$, which boils at 288° (Ber. 16, 2521).

Pyridine, when passed together with hydrogen over reduced nickel at 160°–180°, yields amylamine, not piperidine, and this in poor yield. At higher temperatures ammonia, pentane and lower hydrocarbons are obtained (Sabatier and Mailhe, Compt. rend. 1907, 784).

Pyridine may advantageously be employed as a halogen carrier in halogenation of aromatic compounds (Cross and Cohen, Chem. Soc. Proc. 1908, 15).

The compound of pyridine with methyl iodide, when added to a solution of the necessary amount of iodine in alcohol, is converted into pyridine methylpentiodide $C_5H_5N(MeI)I_4$, melting at 47·5°. Various other periodides are described by Prescott and Trowbridge (J. Amer. Chem. Soc. 1895, 859).

Double compounds with zinc bromide, nickel bromide, copper bromide, and silver iodide, are formed, but are rather unstable (Compt. rend. 1891, 622).

The physiological action of pyridine is similar to that of piperidine, but more energetic. Both produce paralysis of the motor nerves, by their effect on the motor centres. There are also destructive changes in the blood corpuscles, and paralysis of the heart, especially in pyridine poisoning (Chem. Soc. Abstr. 1891, 603). It is excreted as methylpyridylammonium hydroxide (Chem. Soc. Abstr. 1893, ii. 544).

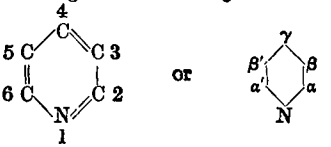
The double compound of pyridine with silver nitrate $AgNO_3{\cdot}2C_5H_5N$ has been recommended by Witt as a ripening agent for photographic emulsions (J. Soc. Chem. Ind. 1904, 235). Lüppe-Cramer, however, denies that it has any advantages over the ordinary ammonia ripening (*ibid.* 1906, 197).

Sulphurous acid esters of pyridine, which may be obtained by heating under a reflux condenser with excess of a bisulphite solution, are useful in the preparation of dyestuffs, and are also used as medicaments (D. R. P. 208638).

On heating pyridine with concentrated sulphuric acid to 300°, β-pyridine-sulphonic acid is obtained. The sodium salt of this acid, distilled with potassium cyanide, yields β-pyridyl cyanide, which on hydrolysis forms nicotinic acid.

Pyridine may be estimated in aqueous solution by heating with excess of gold chloride and dilute HCl, evaporating to dryness and heating the ppt. after repeated washing with pure dry ether. The ppt. has the composition $C_5H_5N{\cdot}HCl{\cdot}AuCl_3$ (Compt. rend. 1903, 324).

Pyridine can be represented as a benzene ring in which one CH group is replaced by nitrogen according to the following scheme :—



The positions 2, 6, and 3, 5 are known as ortho- and meta-, and 4 as the para- position. Hence three mono- derivatives of pyridine are possible. The position of the substituting groups in these isomerides has been proved by means of the phenylpyridines obtained from the naphthaquinolines (Monatsh. 4, 437; Ber. 17, 1518).

Hydroxy- Derivatives of Pyridine.

The three possible hydroxypyridines are known :—

α-Hydroxypyridine, α-pyridone, by distilling the silver salt of hydroxyquinolinic acid; melts at 107°, and is coloured red by ferric chloride.

β-Hydroxypyridine is formed from the β-sulphonic acid by fusing with potash. It melts at 123°, and is also coloured red by ferric chloride.

γ-Hydroxypyridine or **γ-pyridone** (which is probably not a hydroxyl- but a carbonyl- compound) is obtained from hydroxypicolinic acid with evolution of CO_2. It melts at 148° or at 62° in the hydrated form, and is coloured yellow by ferric chloride (Ber. 17, Ref. 169).

Pyridine Monocarboxylic Acids $C_5NH_4(CO_2H)$.

α-Pyridinecarboxylic acid (2- or ortho-), *picolinic acid* was first obtained by oxidising α-picoline. It is easily soluble in water, crystallises in white needles, melts at 137°, and sublimes. By the action of sodium amalgam, ammonia is given off with the formation of an acid $C_5H_5O_3$ (oxysorbinic acid).

β-Pyridinecarboxylic acid (3- or meta-), called *nicotinic acid* from the fact of being first obtained by oxidising nicotine, is also obtained from β-methyl- or ethyl-pyridine, from β-pyridyl cyanide, and from three dicarboxylic acids of pyridine (quinolinic acid, cinchomeronic acid, and *iso*cinchomeronic acid), which on heating give off carbon dioxide. It crystallises in needles and melts at 232°.

γ-Pyridinecarboxylic acid (4- or para-), *iso-nicotinic acid* is obtained from cinchomeronic acid and 2 : 4-pyridinedicarboxylic acid on heating. It melts at 299·5° with sublimation or at 315° in a closed tube, and crystallises from hot water in fine needles.

HYDROXYPYRIDINE-MONOCARBOXYLIC ACIDS.

Several of these acids have been prepared either synthetically, *e.g.* by heating komanic acid $C_6H_4O_4$ with ammonia, or from the dicarboxylic acids by splitting off 1 mol. of carbon dioxide (Ber. 17, 589).

Komenaminic acid $C_5NH_2(OH)_2COOH,2H_2O$ is obtained by boiling komenic acid $C_5H_4O_5$ with ammonia. It decomposes at 270° into carbon dioxide and dihydroxypyridine.

PYRIDINE-DICARBOXYLIC ACIDS $C_5NH_3(CO_2H)_2$.

Quinolinic acid ($\alpha\beta$- or 2 : 3-) is formed by oxidising quinoline. It decomposes and softens at 190°–195°, solidifies at 200°, and melts again at 231°. It decomposes on heating into carbon dioxide and nicotinic acid.

Cinchomeronic acid ($\beta\gamma$- or 3 : 4-) is formed by the oxidation of the quinine alkaloids with nitric acid, or from $\beta\gamma$-methylpyridinecarboxylic acid on oxidation with permanganate. It melts at 259°, decomposing into carbon dioxide, γ-pyridinecarboxylic acid, and some nicotinic acid.

Lutidinic acid ($\alpha\gamma$- or 2 : 4-) is obtained, together with some *iso*cinchomeronic acid, by oxidising lutidine. It melts at 239°–240° (Voigt, Annalen, 228, 54), 235° (Ladenburg, Annalen, 247, 27), decomposing into carbon dioxide and γ-pyridinecarboxylic acid.

***Iso*cinchomeronic acid** ($\beta\alpha'$-) melts at 236°, decomposing into carbon dioxide and nicotinic acid (Werdel and Herzig, Wiener Akad. B. 1879, 825).

Dicarboxylic acid ($\beta\beta'$-) or **Dinicotinic acid.** By heating to 150° *s*-pyridine tetracarboxylic acid obtained by oxidising the lutidincarboxylic acid, prepared by the condensation of *iso*butaldehyde ethylacetoacetate and ammonia. The acid does not melt at 285° (Hantzsch and Weiss, Ber. 1886, 19, 284.

Dicarboxylic acid ($\alpha\alpha'$-) or **Dipicolinic acid.** Obtained by oxidising 2 : 6-dimethylpyridine. It melts at 243° (Epstein, Annalen, 231, 32).

HYDROXYPYRIDINE-DICARBOXYLIC ACIDS $C_5NH_2(OH)(CO_2H)_2$.

Hydroxyquinolinic acid [$OH : (CO_2H)_2 = (\alpha' : \alpha : \beta)$]. By fusing quinolinic acid with potash. It blackens without melting at 254° (Ber. 16, 2158). Heated with water to 195° it decomposes into carbon dioxide and hydroxypyridinecarboxylic acid. Its silver salt on heating yields α-hydroxypyridine (Ber. 17, 590).

Ammoniochelidonic acid is obtained by heating chelidonic acid with ammonia.

PYRIDINE-TRICARBOXYLIC ACIDS $C_5NH_2(CO_2H)_3$.

$\alpha\beta\gamma$-Tricarboxylic acid, Carbocinchomeronic acid, is formed by completely oxidising the quinine alkaloids, also from γ-methylquinoline and from γ-quinolinecarboxylic acid. It loses $1\frac{1}{2}H_2O$ (of crystallisation) at 115°–120°, and melts, if quickly heated, at 250° (Annalen, 204, 308).

$\alpha\beta\beta'$-Tricarboxylic acid, carbodinicotinic acid, is obtained from β-quinolinecarboxylic acid. It melts at 323° (Annalen, 241, 11).

The six tricarboxylic acids theoretically possible are known and characterised.

PYRIDINE-TETRACARBOXYLIC ACIDS $C_5NH(CO_2H)_4$.

$\alpha\beta\alpha'\beta'$-Tetracarboxylic acid. By oxidising the lutidinedicarboxylic acid formed by the condensation of *iso*butylaldehyde with ethyl acetoacetate and ammonia (Hantzsch and Weiss, Ber. 19, 284).

The acid obtained by oxidising collidinemonocarboxylic acid crystallises with 2 molecules of water and melts at 110°. The dried acid melts at 155° (Annalen, 225, 133).

Pyridine-pentacarboxylic acid $C_5N(CO_2H)_5$ from trimethylpyridine-dicarboxylic acid. Crystallises from water with $3H_2O$. Decomposes without melting about 200°.

HALOGEN DERIVATIVES OF PYRIDINE.

α-Chloropyridine results from the action of PCl_5 on α-hydroxypyridine; is an oil boiling at 166°/714 mm. (Ber. 1891, 3150).

β-Chloropyridine. By the action of chloroform or carbon tetrachloride on potassium pyrrol (Ber. 14, 1153) is an oil; b.p. 148°/743 mm.

Dichloro- and trichloro-pyridine are known.

A *dibromopyridine* ($\beta\beta'$) has been obtained by acting on collidine-dicarboxylic acid with bromine and afterwards removing the carboxyl-groups (Pfeiffer, Ber. 20, 1349). It is identical with that obtained by acting on pyridine with bromine (Hofmann, Ber. 12, 988).

HOMOLOGUES OF PYRIDINE.

Picoline (*α-methylpyridine*) $C_5NH_4(CH_3)$. This base is separated from that portion of bone oil which boils between 130° and 145°. On subjecting this to redistillation, the greater part of the oil comes over between 133° and 139°. It is not possible to effect a separation of the bases by means of fractional distillation, but a difference in the solubility of the platinum salts of the two bases furnishes a means of separating them. According to Ladenburg (Ber. 1885, 47), commercial picoline consists of three bases: α-methylpyridine, a little β-methylpyridine, and probably $\alpha\alpha'$-dimethylpyridine. The same observer (Ber. 1885, 51) has also noticed the presence of pyridine in this fraction. It can be separated by means of its picrate, which melts at 162°.

Picoline boils at 128·8°/760 mm.; is an optically inactive oil, and on oxidation yields picolinic acid (*v. supra*).

β-Methylpyridine boils at 143·5°, and on oxidation yields nicotinic acid. It also differs from the α-derivative in being slightly lævorotatory. Landolt shows this effect to be due to errors in manipulation (Ber. 1886, 157).

γ-Methylpyridine does not appear to be contained in bone oil. It has been obtained synthetically by the action of heat on acroleïn-ammonia, and also from allyl tribromide; b.p. 143·1°/760 mm.

PICOLINE-MONOCARBOXYLIC ACIDS $C_5NH_3(CH_3)CO_2H$.

Picolinecarboxylic acid (*pyridine-α-methyl-γ-carboxylic acid*) is formed from uvitonic acid, the product of condensation of pyruvic acid and ammonia. It sublimes without melting, and yields on oxidation $\alpha : \gamma$-pyridinedicarboxylic acid.

$\beta\gamma$-Methylpyridine carboxylic acid ($CH_3 : CO_2H = \gamma : \beta$) is obtained by heating methylquinolinic acid to 180°–185°. It melts at 212° (Ann. Chim. Phys. [5] 27, 493), and yields on oxidation cinchomeronic acid.

Six of the ten possible picoline monocarboxylic acids are known and characterised.

PICOLINE-DICARBOXYLIC ACIDS
$C_5NH_3(CH_3)(CO_2H)_2$.

Methylquinolinic acid ($(CO_2H)_2 : CH_3 = a\beta\gamma$). By oxidising γ-methylquinoline with permanganate. It melts at 186°, giving carbon dioxide and γ-methyl-β-pyridine-carboxylic acid.

Uvitonic acid [$(CO_2H)_2 : CH_3 = a\gamma a'$] is the condensation product obtained from pyruvic acid and alcoholic ammonia. It melts at 274°, splitting up into carbon dioxide and picoline-carboxylic acid.

Picoline-dicarboxylic acid, from aldehydine, the condensation product of ethylidene chloride and aldehyde ammonia. It sublimes easily without melting.

Three other isomerides are known.

A picoline-tetracarboxylic acid is also obtainable from the dicarboxylic acid of collidine by oxidation of the methyl- groups with permanganate. Lutidine-tricarboxylic acid is formed as an intermediate product.

Lutidine (*dimethylpyridine*). The bases having this constitution are mainly contained in that portion of the basic oil boiling between 150°–170°. After redistilling, it is separated into the two fractions 150°–160° and 160°–170°. The position of the methyl groups in these two fractions is determined by means of the oxidation products formed. The first fraction yields on oxidation *iso*cinchomeronic acid, which melts at 236°. On heating, carbon dioxide is split off and nicotinic acid is formed. From this is inferred that the position of the two methyl groups is $a'\beta$. The higher fraction yields lutidinic acid on oxidation, and this, on heating, gives *iso*nicotinic acid, from which it follows that the methyl- groups have the positions $a\gamma$. All the acids give pyridine on distillation with lime. According to the researches of Ladenburg and Roth (Ber. 18, 49), the fraction 139°–142° also contains a lutidine, which was separated by means of the mercuric chloride salt, melting at 186°. This was decomposed with potash, and distilled, when, after drying, an oil was obtained which boiled at 142°–143°, and yielded on oxidation with permanganate a dibasic acid which is identical with that obtained from synthetical lutidine prepared by condensing cinnamic aldehyde, ethyl acetoacetate, and ammonia (Epstein, Annalen, 231, 1). Its sp.gr. is 0·9545, and b.p. 143°.

The constitution of the β-lutidine is

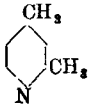
(Ladenburg and Roth).

Lutidine-monocarboxylic acid (*aa'-dimethylnicotinic acid*). Obtained by distilling lutidine-dicarboxylic acid (Weiss, Ber. 19, 1308). It crystallises in fine needles melting at 160°.

Lutidine-dicarboxylic acid. Obtained by the condensation of *iso*butylaldehyde, ethyl- acetoacetate, and ammonia (Engelmann, Annalen, 231, 51; Hantzsch and Weiss, Ber. 19, 284).

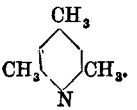
Lutidine-tricarboxylic acid is formed by the oxidation of collidine-dicarboxylic acid with permanganate.

α-Lutidine (2 : 4-*dimethylpyridine*). Separated by adding mercuric chloride to a solution in hydrochloric acid of the bases boiling at 158°–160°. The salt has the composition $C_7H_9N,HCl,2HgCl_2$, and melts at 127°. On distilling with potash, the salt is decomposed, and the base, after drying, boils at 157°. Its sp.gr. is 0·9493 at 0°/4°. It yields a pyridine-dicarboxylic acid on oxidation with permanganate, and the acid melts at 235°. This is known as α-lutidinic acid or αγ-pyridine-dicarboxylic acid, since on heating carbon dioxide is given off and *iso*nicotinic acid is formed. Hence α-lutidine has the composition



(Ladenburg and Roth, Ber. 18, 913).

Collidines (*γ-collidine, trimethylpyridine*)
$C_5NH_2(CH_3)_3$
may be prepared by distilling collidine dicarboxylic ester (obtained by oxidising the condensation product of aldehyde ammonia and ethyl acetoacetate) with lime. It boils at 171°–172°, and has the constitution



A base, $C_8H_{11}N$, has been isolated from the fraction of bone oil boiling between 170° and 180°, but this has been shown by Weidel and Pick to be a 2-methyl-4-ethylpyridine from the fact of its giving on oxidation lutidinic acid melting at 219°. The base is more soluble in cold than in hot water. Its sp.gr. is 0·9286 at 16·8°; it boils at 177·8°/758 mm. (Weidel and Pick, Monatsh. 5, 656). These authors are of opinion that Anderson's collidine (Phil. Mag. 4, 9, 145, 214) was impure. The base does not form any crystallised salts, and is not identical with any synthetical collidine.

Aldehydine (2-*methyl*-5-*ethylpyridine*). Formed by the condensation of ethylidene chloride with ammonia (Dürkopf, Ber. 18, 921). It boils at 176°, and has sp.gr. 0·9389 at 0°/4°.

Collidine dicarboxylic acid is obtained by oxidising hydrocollidine-dicarboxylic acid with nitrous acid. The ether of the latter acid is the product of condensation of ethyl acetoacetate with aldehyde ammonia. It yields on heating with lime $aa'\gamma$-trimethylpyridine. The acid yields by successive oxidation of the methyl- groups by permanganate the following carboxylic acids:

Lutidine-tricarboxylic acid
$C_5N(CH_3)_2(CO_2H)_3$,

Picoline-tetracarboxylic acid
$C_5N(CH_3)(CO_2H)_4$,

Pyridine-pentacarboxylic acid $C_5N(CO_2H)_5$.

If one carboxyl- group be removed from the original acid and then it be oxidised, the following acids are successively obtained:—

From collidine-monocarboxylic acid $C_5NH(CH_3)_3CO_2H$ the acids lutidine-dicarboxylic acid $C_5NH(CH_3)_2(CO_2H)_2$, picoline-tricarboxylic acid $C_5NH(CH_3)(CO_2H)_3$, pyridine-tetracarboxylic acid $C_5NH(CO_2H)_4$.

Piperidine, hexahydro-pyridine, is obtained in small quantity by the reduction of pyridine with tin and hydrochloric acid (Königs, Ber.

1881, 14, 1856). A better yield is obtained by operating in absolute alcoholic solution with sodium. It may be prepared from pyridine in 95 p.c. yield by electrolytic reduction (E. Merck, D. R. P. 90308; Pip, Eng. Pat. 21471). It may also be prepared by heating piperine, obtained from pepper, with soda lime. It is a liquid smelling like pepper and ammonia, boiling at 105·7°, sp.gr. 0·8810 at 0°. Miscible in all proportions with water. It combines with quinones to form dyes.

Its combination with hydroquinone, pyrocatechin, and several other phenols, has been patented by Joseph Turner & Co., Ltd. (D. R. P. 98465).

An account of the physiological action of piperidine and allied compounds is given by Wolffenstein (Ber. 34, 2410). Its chemical reactions have been the subject of special study by Oechsner (Bull. Soc. chim. 43, 177).

Piperidine guaiacolate prepared by the action of piperidine on guaiacol dissolved in benzene or petroleum melts at 79·8°. It is used in the treatment of phthisis (Pharm J. 1897, 81), and is important as combining the properties of a strong vascular and nervine tonic—piperidine—with an antiseptic guaiacol (Tunnicliffe, Chem. Soc. Trans. 1898, 145).

Various derivatives of piperidine have been synthesised by Ahrens (Ber. 1898, 2278).

Quinoline. *See* QUINOLINE.

COLOURING MATTERS DERIVED FROM BONE-OIL BASES.

1. **From Pyrrol.** A red dye may be obtained from pyrrol by treating cotton cloth, after dipping in a weak alcoholic solution of bitter almond oil (benzaldehyde), with alcoholic pyrrol solution, hydrochloric acid, ferric chloride, and gently warming. A black colour is obtained by substituting cinnamon oil (cinnamic aldehyde) (Chem. Zeit. 1890, 348).

Pine wood may be dyed red by moistening with hydrochloric acid, and treating with the vapour of pyrrol.

Pyrrol blue may be obtained in two varieties: (*a*) by mixing pyrrol and isatin (1 mol. of each) in sulphuric acid, yielding the 'A' variety; and (*b*) by operating in acetic acid under specified conditions, when pyrrol blue 'B' is obtained with a certain amount of A. Pyrrol blue B has a metallic lustre, and is much less soluble than pyrrol blue A. Pyrrol blue A cannot be acetylated, but on treating pyridine solution with acetic anhydride a small amount of the pyrrol blue B derivative is obtained. This acetyl derivative dissolves in sulphuric acid to a magenta solution, which rapidly changes to a cornflower blue, owing to the formation of a disulphonic acid. This acid is very soluble in water and dyes silk blue (Liebermann and Häse, Ber. 1905, 2847; *see* also Ber. 17, 1034).

2. **From Pyridine.** Pyridine dyestuffs may be obtained by diazotising aminobenzylpyridine, and combining with the usual components. Aminobenzylpyridine is obtained by reducing the nitro- compound produced by the condensation of nitrobenzyl chloride and pyridine bases. These products dye tannin-mordanted cotton, or wool and cotton from an acid-bath (Farb. vorm. Meister, Lucius and Brüning, Eng. Pat. 4545).

When mixtures of pyridine (1 mol.) and aromatic amines (2 mols.) are acted upon by cyanogen chloride or bromide dyestuffs are formed practically quantitatively and very pure, with the elimination 1 mol. of cyanamide. They crystallise well, and vary from yellow, through orange and red, to violet, and dye silk in shades showing fine fluorescence; and some show marked affinity for unmordanted cotton. They are soluble in water with difficulty, more readily in acetic acid and alcohol, and in pyridine (W. König, J. pr. Chem. 1904, 105).

3. **From Piperidine.** The quinones (benzo-, tolu-, naphtha-, phenanthra-quinones) interact with piperidine, yielding colouring matters which are readily changed by acids and alkalis. The compound with benzoquinone $C_6H_2O_2(NC_5H_{10})_2$ forms thick, reddish-violet prisms with blue reflex, melting at 178°. Neutral or alkaline solutions are blood-red, acid solutions carmine (Lachowicz, Monatsh. 1888, 505).

Isatin blue is derived from piperidine as follows: Dipiperidyl isatin is prepared by heating an alcoholic solution of isatin (1 mol.) with (2 mols.) piperidine on the water-bath for an hour, and crystallising from alcohol. Isatin blue results from heating this compound to 125°–160° in a current of air, or by agitating with acetic anhydride at 60° for some time and pouring into water. It forms indigo-blue solutions in alcohol, ether, or acetic acid, and is insoluble in benzene or chloroform. It may be heated without change to 160°, but is completely decomposed at 230° (Schotten, Ber. 1891, 1366).

p-Aminophenyl piperidine, which may be compared with *p*-aminodimethyl aniline, reacts in many cases in a similar way to this compound. When oxidised with a primary, secondary, or tertiary amine, *indamines*, varying from blue to green are produced. Oxidised in the presence of meta-diamines, compounds may be precipitated by means of zinc chloride which dye cotton blue.

With phenol, when oxidised with the theoretical quantity of potassium ferricyanide, a blue indophenol is obtained. With naphthols violet colours result. Other colours are also described by Lellmann and Geller (Ber. 1888, 2287).

Literature.—Anderson, Trans. Roy. Soc. Edin. 16, 463; 20, 247; 21, 219; 21, 571; Annalen, 70, 32; 84, 44; 94, 358; 105, 335; Weidel, Sitz. Ber. 79, 837; 80, 443; 80, 821; 81, 512; 90, 972; Ciamician, Ber. 1904, 4200–4255; Bamberger, Ber. 1891, 1758; and in general the papers of the following: Ciamician, Dennstedt, Hoogewerff and van Dorp, Liebermann, Oechsner de Coninck, and Weidel.

BONE PHOSPHATES *v.* FERTILISERS.

BOOKUM or SAPPAN WOOD. An Indian wood, the product of *Cæsalpinia Sappan* (Linn.). Used in dyeing reds.

BOOMAH NUTS. The fruit of *Pycnocoma macrophylla* (Benth.), belonging to the Euphorbiaceæ. Used in tanning (Holmes, Pharm. J. [3] 8, 363).

BORACIC or BORIC ACID *v.* BORON.

BORACITE *v.* BORON.

BORAL *v.* SYNTHETIC DRUGS.

BORATES *v.* BORON.

BORAX. As a mineral, borax ($Na_2B_4O_7$,

$10H_2O$) is found as an efflorescence and as monoclinic crystals, sometimes of considerable size, on the shores of the salt lakes of Tibet and California. In San Bernardino and Lake counties in California there are several places known as 'Borax Lake'; but most of the borates commercially mined in this region belong to other species (ulexite, colemanite, &c.). The Tibetan deposits extend from the lake-plain of Pugha in the west to the lakes of Tengri Nur in the east, and formerly, since very early times, much crude material was exported under the name of tincal. (*v.* BORON.) L. J. S.

BORDEAUX *v.* AZO- COLOURING MATTERS. Lambert (Zeitsch. anal. Chem. 22, 46) detects this dye in wines by precipitating with basic lead acetate, and extracting the precipitate with alcohol; the red solution thus obtained is turned yellow by alkalis. Wool heated with the wine withdraws its colouring matters.

Bellier (J. Pharm. Chim. [5] 14, 7) describes a method of determining quantitatively the amount of this dye in wines.

BORDEAUX MIXTURE *v.* PLANT SPRAYS.

BORNEO CAMPHOR *v.* CAMPHORS.

BORNEOL *v.* CAMPHORS; TERPENES.

BORNEO TALLOW is a generic term for a large variety of fats obtained from the kernels of a number of plants belonging to the *Dipterocarpus* family, such as *Shorea stenoptera* (Burck.), *Shorea aptera* (Burck.), *Hopea aspera* (de Vriese), *Pentacme siamensis* (Kurz), all of which are indigenous to the Sunda Islands, Indo-China, and the Malay States. All the fats derived from these trees are also in commerce known under the native name of Minjak Tangkawang (Tangkawang Fat). Minjak Tangkawang represents a mixture of at least six fats, obtained from six varieties of trees known to the natives as Tangkawang toengkoel, T. rambei, T. lagar (these trees have a diameter of more than 3 ft.), T. goentjang (growing in swampy regions, and reaching a height of 22 ft., whilst the diameter of the trunk rarely exceeds 6 inches), T. madjan, T. terindak.

The fat is prepared by the natives in a very crude manner. In the 'wet process' the fruits are placed in baskets, immersed in water, and left therein for from 30 to 40 days. After that time the shells are removed, the kernels are split into four parts, and these spread on boards, exposed to the sun to dry. The dried fruit is then pounded, boiled with water, and the liquid fat skimmed off and moulded in the internodes of bamboo stems; hence the commercial samples have a cylindrical shape. The 'dry process' consists in cutting the kernels into discs immediately after the fruit has been collected, drying the discs by exposure to the sun, and subsequently pressing. The fat obtained by the dry process yields the best product, which is largely used for edible purposes in the East. The Shorea fruit (erroneously also described in the Straits Settlements as Illipé Nut) has been occasionally shipped to Europe and endeavours have been made to convert it into a 'chocolate fat,' but as the harvest is a remunerative one only in intervals of several years, this manufacture has been abandoned. Borneo tallow contains considerable quantities of stearic acid. Samples examined in the writer's laboratory contained as much as 66 p.c. of stearic acid. The fat melts at 35°–36° and liquefies completely at 42°. The insoluble fatty acids have a high melting-point, viz. 53°–54°, and seem to consist of 66 p.c. of stearic acid and 34 p.c. of oleic acid.

The fats from *Shorea Ghysbertiana* and from *Isoptera bornensis* have been described recently as Enkabang fat and Teglam fat respectively (Brookes, Analyst, 1909, 206).

J. L.

BORNESIT *v.* GLUCOSIDES.

BORNITE. A sulphide of copper and iron, of importance as an ore of copper (Cu 45–71 p.c.). On a freshly fractured surface the colour is dark bronze, but this quickly tarnishes to purple or deep reddish; hence the names purple copper-ore, variegated copper-ore, erubescite, and the Cornish miner's name horse-flesh-ore. Further alteration produces a black sooty coating. The massive ore is always much intermingled with copper-pyrites, and even the rarely occurring cubic crystals usually contain a nucleus of copper-pyrites. The exact composition of the mineral has therefore long been doubtful; analyses by B. J. Harrington (1903) of carefully selected material gave the formula Cu_5FeS_4. This is the bornite of W. Haidinger (1845): bornite of F. S. Beudant (1832) is an obsolete synonym of tetradymite or telluric bismuth. L. J. S.

BORNYVAL. Pharmaceutical name for the *iso*valerianic ester of borneol $C_{10}H_{17}O.C_5H_9O$, a limpid fluid smelling like valerian, insoluble in water, freely soluble in alcohol or ether; b.p. 255°–260°; sp.gr. 0·951 at 20°, $[D]_{20}=27°\,40'$.

BORO-GLYCERINE. An antiseptic, patented by Barff (D. R. P. 18108; Eng. Pat. 5906, 1884); prepared by heating 92 parts glycerol with 62 parts of boric acid at 200°. It is a yellowish, transparent substance, soluble in alcohol and in 40 parts of water. Used as a preservative for fruits and wines (J. Soc. Chem. Ind. 1, 244; 4, 362).

BORON. B. At. wt. 11·0. An element usually reckoned among the metalloids, although it presents analogies to the metals, and has been placed by Etard (Compt. rend. 91, 627) at the head of the vanadium group, intermediate between the places of phosphorus and carbon; is a triad in most of its known combinations, but is also capable of acting as a pentad (Michaelis and Becker, Ber. 13, 58). Never occurs free; usually as boric acid, and in several minerals, as *borax* or *tincal*, *boracite*, *hydroboracite*, *rhodizite*, *sassolin*, *borocalcite*, *boronatrocalcite*, and *botryolite*, and in small quantities in *schorl*, *datolite*, *tourmaline*, *apyrite*, and *axinite*.

The element was first isolated by Gay-Lussac and Thénard in 1808, by heating boric oxide with potassium. According to Wöhler and Deville (Ann. Chim. Phys. [3] 52, 63), it may be obtained by mixing 60 grams of sodium in small pieces with 100 grams of powdered boric oxide in an iron crucible, covering the mixture with a layer of 30 grams ignited sodium chloride in fine powder, and heating the whole to redness. After the completion of the reaction, which is very violent, the mixture is stirred with an iron rod, until the sodium and sodium chloride are fused, and carefully poured into dilute hydrochloric acid, and the residue washed with water containing ammonium chloride (which salt

is subsequently removed by alcohol) and dried. Boron can also be obtained by heating potassium borofluoride with potassium (Berzelius), or magnesium (Wöhler and Deville); by the electrolysis of fused boric oxide (Davy); by reducing boron trichloride by hydrogen (Dumas); by fusing borax with amorphous phosphorus (Dragendorff); by heating boric oxide with magnesium and treating the residue with dilute hydrochloric acid.

Wöhler and Deville's method gives a product containing, in addition to boron, compounds of boron with sodium, iron, and hydrogen, and boron nitride. The best method is that of Moissan. Pure and dry boric oxide is intimately mixed with as much magnesium filings as will suffice to reduce one-third of it. The mixture is placed in an earthenware crucible in a furnace at a bright-red heat, when the reaction proceeds at once rather violently. Heating is continued for ten minutes and the mass allowed to cool. The middle portion of the mass, which is of a reddish colour, is mechanically separated from the surrounding black portion as completely as possible, and boiled with a large excess of dilute hydrochloric acid which removes the boric acid and borides of magnesium.' The magnesium borate is removed by repeated boiling with strong hydrochloric acid; and the silica (resulting from the disintegration of the crucible) by heating the residue in a platinum vessel with hydrofluoric acid. The residue is washed by decantation with water and dried. It is then approximately pure, but still contains a small quantity of a magnesium boride which cannot be got rid of except by fusing the product with about fifty times its weight of boric oxide, and repeating the above operations.

Boron has been produced by Weston and Ellis (Trans. Faraday Soc. 1907, 170) by the action of aluminium powder on boric oxide. If 2 mols. of boric oxide to 2 atoms of aluminium are used, the chief product is boron, but with a smaller proportion of boric oxide aluminium boride is produced to a large extent.

Boron may be prepared electrolytically as follows: A fused metallic borate is electrolysed between carbon poles separated so as to prevent the boron floating to the cathode. By the use of a high-current density at the anode sufficient heat is generated to effect the reduction of the boric oxide which collects there (U. S. Pat. 785962).

Commercial boron is purified by grinding the product obtained by heating boric oxide and magnesium with hydrochloric acid, and quickly pouring off the upper liquid. This contains matter in suspension which holds a higher proportion of impurities than does the residue at the bottom. This process of 'fractional decantation' is repeated several times. The residual boron, which may still contain boron hydride, magnesium boride, boric oxide, and a borate, is compressed into a thick stick or cake, and heated to 1200° in a vacuum electric furnace, which either volatilises or dissociates all these impurities. The pure boron is then melted down in the arc in a current of inert gas, preferably hydrogen. The resulting boron is a dense solid substance which conducts electricity and is completely fusible without apparent volatilisation (British Thomson-Houston Co., Eng. Pat. 1197, 1907).

Pure boron is a chestnut-coloured powder which can be compressed into a fairly consistent solid. It has a density of 2·45, and is infusible at the temperature of the electric arc (Moissan); it is tasteless, odourless, staining the fingers strongly; becomes denser on being heated in a vacuum or in gases which have no action upon it; not oxidised at ordinary temperatures in either air or oxygen; heated in air, it burns with a reddish light, forming B_2O_3 and BN; burns with dazzling brightness in oxygen, forming B_2O_3. Boiling water has no action on it, but it is readily oxidised by strong nitric acid in the cold, and by sulphuric acid when heated. When heated to redness with the alkaline salts of oxyacids, yields an alkaline borate, the formation being frequently attended with incandescence, and in the case of nitre with explosion. Heated with potash it forms potassium borate with liberation of hydrogen, and reduces the chlorides of lead, gold, mercury, and silver, and sulphide of lead, chloride or sulphide of boron being formed (Wöhler and Deville, *l.c.*; and Annalen, 105, 72). Heated in nitrogen, it forms white boron nitride. It decomposes nitric oxide at a red heat, burning brilliantly and forming boric oxide and nitride, but apparently has no action on nitrous oxide.

Crystalline boron. This variety has never been obtained in a state of purity, but always contains a small proportion of carbon or aluminium or both. It may be obtained by placing 8 parts of aluminium with 10 parts of fused boric acid in a gas-carbon crucible filled up with ignited charcoal and placed inside another crucible of graphite which is heated to 1500°, for five hours. The aluminium is removed from the resulting mass by means of fairly strong soda, and the residue is then boiled out with hydrochloric and hydrofluoric acids. The residue contains some alumina which is separated mechanically as far as possible, and completely by glacial phosphoric acid. Crystals may also be obtained by heating 2 parts of fused and powdered borax with 1 part of magnesium. A commercial process has been patented by Kühn (Chem. Zentr. 1904, i. 64). Boron compounds are mixed with sulphur and aluminium, and the mixture, which burns, ignited. Crystals of boron are found in the resulting mass, and are separated from it by extraction with water, which decomposes the aluminium sulphide, forming aluminium hydroxide and H_2S, and leaving the crystals of boron.

The hardest variety of crystalline boron contains 2·4 p.c. of carbon (Wöhler and Deville, Joly). It consists of metallic-looking leaves which are black and opaque, or red in very thin sections. It is only oxidised with very great difficulty in oxygen, and in air no change takes place even at 2000°. Molten potash or lead chromate oxidises it with incandescence, but fused potassium nitrate does not affect it. 'Boron diamonds' of the composition $B_{48}C_2Al_2$ are colourless, transparent prisms (Hampe) of the tetragonal system, and a still more highly refracting variety was prepared by Wöhler and Deville.

Boron may be introduced into steel, and the properties of the boron steel so obtained have

been studied by Osmond (Compt. rend. 110, 242, and 346), by Moissan and Charpy (*ibid.* 120, 130), and by L. Guillet (*ibid.* 144, 1049). Boron steels are obtained either by heating amorphous boron with reduced iron in a current of hydrogen, or by adding crystalline boron to the molten metal. On hardening by heating to a known temperature and quenching, boron steel behaves like a high grade hard carbon steel as regards increase in tensile strength, whilst the diminution in extension is not so great. The hardness of boron steel is not much affected by heating and quenching. The special effect of boron appears to be to communicate to the steel a high tensile strength rather than actual hardness when the metal is heated and quenched.

Boron rapidly reduces manganese oxides in the electric furnace. With excess of oxide products containing up to 97 p.c. manganese may be obtained which are soft enough to be filed. With excess of boron, harder, granular substances result, containing up to 20 p.c. boron. From these a definite boride MnB may be isolated. It is a crystalline metallic powder attacked by halogens and oxygen at high temperatures, and by alkali hydroxides and carbonates at a red heat. Water or steam slowly decomposes it with evolution of hydrogen (Binet du Jassonneix, Compt. rend. 139, 1209). The same author has obtained very similar results with molybdenum dioxide and boron (Compt. rend. 143, 169); and has also prepared two definite borides of chromium Cr_3B_2 and CrB, by fusing together chromium and boron. They are very stable towards reagents, especially the former, but are decomposed by fused alkalis, and by chlorine at a red heat. They are soluble in hydrofluoric, hydrochloric, and concentrated sulphuric acids (Compt. rend. 143, 1149). The same author has also prepared Ni_2B, NiB_2, Co_2B, and CoB_2 (Compt. rend. 145, 240); and borides of zirconium, chromium, tungsten, and molybdenum have been prepared by Tucker and Moody (Chem. Soc. Proc. 1901, 129).

Compounds of Boron with Non-metallic Elements.

Boramide $B(NH_2)_3$ is formed together with ammonium chloride by the action of ammonia on boron trichloride at a low temperature (Joannis, Compt. rend. 135, 1106).

Borimide $B_2(NH)_3$ is a spongy white mass insoluble in most solvents. On heating it begins to give off ammonia at 125°–130°, and is completely transformed into boron nitride at slightly higher temperatures. It is prepared by heating the compound of boron trisulphide and ammonia $B_2S_3,6NH_3$ for some time at 115°–120° in a current of hydrogen or dry ammonia (Stock and Blix, Ber. 1901, 3039; and Joannis, Compt. rend. 135, 1106).

Boron carbide B_6C forms exceedingly hard shining black crystals, which are capable of polishing diamonds. It may be obtained massive by fusing together boric oxide and carbon in an electric resistance furnace and cooling fairly rapidly (E. A. Sperry, U.S. Pat. 869114).

Shaped blocks of boron carbide are obtained by preparing the body of the block in pure carbon, embedding this in powdered carbide, and firing in an electric furnace (Bölling, Eng. Pat. 6693, 1905). Modifications of this process have also been patented (Additions (2) Sept. 30, 1904, to Fr. Pat. 353017).

Boron nitride BN is a white, amorphous, bulky powder. It is infusible, insoluble in water, and generally somewhat inert to reagents, but Stock and Blix (Ber. 1901, 3039) have described another modification which is chemically much more active. It may be obtained mixed with B_2O_3 by burning boron in air; or by the actiod of nitrogen on a mixture of boric anhydride and carbon heated to redness (Wöhler and Deville, Ann. Chem. Phys. [3] 52, 84). It is best prepared by the action of ammonium chloride vapour on a porous mass of calcium phosphate and borax or boric oxide heated to bright redness, afterwards extracting the cold mass with hydrochloric acid and water, and drying the residue of BN in a vacuum desiccator (Moeser and Eidmann, Ber. 1902, 535); or by allowing boron bromide to drop into liquid ammonia, and heating the precipitated mixture of boramide and borimide to 750° in a current of ammonia gas (Stock and Holle, Ber. 1908, 2095).

Boron sulphide N_2S_3 forms fine white needles of density about 1·55, which melt at 310°. It is volatile in hydrogen without decomposition. It has been carefully studied by Moissan (Compt. rend. 115, 203). It may be prepared by heating together sulphur and amorphous boron (Wöhler and Deville); or, better, by heating ferroboron in a stream of dry hydrogen sulphide at 400°, and purifying the resulting product by dissolving out the sulphur with carbon disulphide (Hofmann, Zeit. angew. Chem. 1906, 1362). The latter process is much cheaper than the other.

Boron trichloride BCl_3 is a colourless, very mobile, refractive liquid which fumes in the air. Sp.gr. 1·4338 at 0°; b.p. 18·23° (Regnault). It is decomposed by water with formation of hydrochloric and boric acids. It is prepared by passing dry chlorine over amorphous boron, and collecting the vapours in a U-tube immersed in a freezing mixture. The product is purified by shaking with mercury to remove chlorine, and by fractionation.

Boron tribromide BBr_3 resembles the chloride in physical properties. It is prepared in the same way, substituting bromine for chlorine, or by treating a red-hot mixture of carbon and boric oxide with bromine vapour.

Boric oxide B_2O_3 may be obtained by burning boron in oxygen, or, more easily, by strongly heating boric acid, when it melts at 577° to a viscid mass, cooling to a colourless brittle glass of sp.gr. 1·83. Non-volatile, and hence capable of expelling carbonic, nitric, and sulphuric acids from their salts at a red heat. Soluble in water, forming boric acid.

A blue glass, 'boron-ultramarine,' of colour varying with the duration and intensity of heating, and with the proportions of the ingredients, is made from sodium sulphide and boric anhydride. It is stable in air and only slightly soluble in water (J. Hoffmann, Zeitsch. angew. Chem. 1906, 1089).

Boric or Boracic acid. *Sal sedativum*

Hombergii, Sal narcoticum vitrioli. Boric oxide forms three hydrates:

Orthoboric acid $B_2O_3 \cdot 3H_2O = H_3BO_3$.
Metaboric acid $B_2O_3 \cdot H_2O = H_2B_2O_4$.
Pyroboric acid $2B_2O_3 \cdot H_2O = H_2B_4O_7$.

Boric acid appears to be a dibasic acid, and most of its salts may be regarded as derived from metaboric or pyroboric acid. Both these are so-called 'weak' acids. Their salts, when soluble, have usually an alkaline reaction, even when containing excess of boric acid, and are decomposed even by carbonic acid.

Boric acid is found free in nature in many volcanic districts. In Central Italy it is produced on a large scale in the territories of four communes: Pomerance, Massa Marittima, Castel Nuovo di Val di Cecina, Montieri, all in the province of Tuscany, the nearest shipping point being Leghorn, to which place it is brought by railroad from Volterra. It also occurs in the extinct crater of a volcano on one of the Lipari Islands, and in the crater of Stromboli, an active volcano on another island of the same group, near Sicily. Volcanic emanations containing boric acid occur in Nevada, in California, and Nova Scotia. It exists in solution in the mineral waters of Wiesbaden, Aachen, and Krankenlied, in Germany; in the mud volcanoes of the Colorado Desert, in San Diego county, California; in the water of several mineral springs in Tehama county, California. In smaller quantities it exists in sea water and in the ash of many plants.

Sassolin, or Tuscan boric acid, is never produced in the pure state, but is always associated with impurities, both soluble and insoluble. It differs considerably in quality, some parcels containing 89 p.c. of crystallised acid, while others yield only 75 p.c. The following analyses show its general composition:—

Analyses of crude Tuscan boric acid.

Boric acid B_2O_3	47·95	44·04
Water { combined	37·00	33·98
Water { hygroscopic	0·73	2·80
Ammonium sulphate $(NH_4)_2SO_4$	5·67	10·62
Sulphate of alumina and iron	0·13	0·20
Calcium sulphate	trace	1·20
Magnesium sulphate	6·91	4·03
Sodium sulphate	0·07	1·10
Sodium chloride	0·23	0·32
Sand	0·42	0·80
Sulphur	—	trace
Organic matter	0·89	0·91
	100·00	100·00

An analysis of an average sample taken from 5000 tons shows it to be composed as follows:—

Crystallised boric acid $B_2O_3,2H_2O$	83·5
Hygroscopic water	1·4
Ammonium sulphate	5·3
Magnesium sulphate	7·5
Iron and alumina	0·3
Sand, organic matter, &c.	2·0
	100·0

Boric acid occurs on the West Coast of South America, principally in the form of boronatrocalcite (*ulexite*, or *hayesine*), and is found throughout the province of Atacama and in portions of Chili. Ascotan and Maricunga, to the north of Copiapo, are the places which have proved most successful commercially. The crude material, known as *tiza*, occurs in both places in lagoons or troughs; these, instead of being entirely filled with common salt, as is usually the case in the desert, contain zones or layers of boronatrocalcite, alternating with layers of salt and salty earth. The lagoons of Maricunga are estimated to cover 3,000,000 sq. metres. The raw material contains on the average about 25 p.c. of boric acid, but by washing and calcination it may be raised to 55 or 60 p.c. The roughly purified boronatrocalcite is shipped to England and Germany.

A borate of lime (*rhodizite*) is imported from the West Coast of Africa.

Pure boric acid is easily obtained by treating a solution of 3 parts borax in 12 parts hot water with 1 part sulphuric acid. On cooling, boric acid separates out; it is recrystallised from hot water, dried and fused to expel traces of sulphuric acid, and again recrystallised from water. It forms white, translucent, monoclinic laminæ (Kenngott), which have a mother-of-pearl lustre and are unctuous to the touch. Sp.gr. 1·434 at 15°.

Boric acid evaporates freely in a current of steam. The loss sustained by evaporating an aqueous solution is 0·28 p.c. of the water evaporated, equal to 2·8 lbs. for every 100 gallons.

The solubility of boric acid in water has been determined by Ditte (Compt. rend. 85, 1069), but his results are probably low. Herz and Knoch find considerably higher values at 13°, 20°, 25°, and 26°. The figures of Brandes and Firnhaber (Arch. Pharm. 7, 50) also differ. The results obtained by Nasini and Ageno (Zeitsch. physikal. Chem. 1909, 69, 482) are quoted below:

Temperature	Grams of H_3BO_3 per 100-gram solution	Temperature	Grams of H_3BO_3 per 100-gram solution
0°	2·59	60°	12·90
12·2°	3·69	69·5°	15·58
21°	4·90	80°	19·11
31°	6·44	90°	23·30
40°	8·02	99·5°	28·10
50°	10·35		

The solubility of boric acid in water is lessened (not, as stated in various places, increased) by the presence of hydrochloric acid (Herz, Chem. Zentr. 1903, i. 312) and of sulphuric, nitric, and acetic acids; but tartaric acid has the opposite effect (*ibid.* 755). Boric acid is soluble in alcohol and volatile oils. A cold saturated solution colours litmus a wine-red; a hot saturated solution gives a bright-red colour.

Crystallised boric acid, heated to 100°, is converted into $H_2B_2O_4$ (Schaffgotsch, J. 1859, 71), and into $H_2B_4O_7$ at 160° (Merz, J. pr. Chem. 99, 179; Ebelmen and Bouquet, Ann. Chim. Phys. [3] 17, 63). At a stronger heat the acid froths up, parting with its water and forming boric anhydride as a fused viscid mass, solidifying to a fissured glass on cooling.

Boric acid is extensively used in medicine as an antiseptic; and as a food preservative it is also very widely employed. It is also employed for glazing porcelain, in the preparation

of glass and certain pigments, and for soaking the wicks of stearin candles.

The effect of boric acid in glazes is to increase their hardness and their fusibility, and to modify the coefficient of expansion. A small amount of boric acid lowers the expansion, whilst a large quantity produces an increase. This effect is explained by Grenet (Compt. rend. 123, 891) to be due to the fact that when the proportion of bases to boric acid is high, devitrification occurs, whilst when the boric acid is the more important constituent, the coefficient of expansion tends to approximate to that of boric acid itself, which is higher than that of any glass.

It has also been proposed to use boric acid in the preparation of nitric acid from Chili saltpetre, so as to obtain borax as a by-product.

Industrial extraction of boric acid. The occurrence of the *sal sedativum* of Homberg in the water of the Tuscan lagoons appears to have been first noticed in 1777 by Höfer, a Florentine apothecary, and its extraction was begun about 1815, and to-day a large part of the boric acid of commerce is derived from the lagoons near Monte Rotondo, Lago Zolforeo, Sasso, and Larderello, in the Maremma of Tuscany, inclosing both natural and artificial vents. The *soffioni* or jets of steam, which often rise in thick columns to a considerable height, contain only traces of boric acid, but when these are condensed in the water of the lagoons this becomes gradually charged with the acid which is obtained from the solution by evaporation.

To obtain the boric acid, the soffioni are surrounded by basins of rough masonry, several of which are arranged in steps, one above the other, in such manner that the contents of each basin can be led by gravitation into the basin below. Fresh water from a neighbouring spring is conducted into the uppermost basin, whilst the gases and vapours of the fumaroles rise through the water from beneath, occasionally with such violence as to eject the water to a height of several feet. After twenty-four hours the water in the first basin, which is generally muddy, is allowed to pass into the second basin, the first being recharged with fresh water. After another twenty-four hours the second basin is discharged into the third and the first into the second, the second and following basins being also built round soffioni. After having passed through four or five of these basins, the solution is passed into rectangular reservoirs in which the suspended matter is deposited on standing. From these it passes into a series of leaden evaporating pans, placed in couples one above the other in the form of a terrace. These pans are heated by the gases and vapours of soffioni which, on account of their situation, are otherwise useless—by a method first adopted by Count Lardarel in 1815. The evaporating pans are square, about 1 foot deep and 9 feet square, and are supported on wooden beams. The solution is heated in these for twenty-four hours until it has attained a density of 1·017, when it is decanted into a second series of pans, where, after another twenty-four hours, it attains a density of 1·034, and is finally decanted into the last four pans, where it is evaporated to a specific gravity of 1·07.

The temperature gradually increases, being in the first pans about 60° to 70°, in the following pans about 75°, and in the last as high as 80°.

In all these pans a precipitation of gypsum takes place, which requires to be removed from time to time. When the solution in the last pans has attained a density of 1·07, it is run through funnels into the crystallising vats, consisting of wooden tubs lined with lead. After twenty-four hours the crystallisation is complete, the mother liquor is then decanted off and added to the evaporating pans a few hours before the completion of the concentration. The crystals are drained in baskets placed under the crystallising vats for twenty-four hours, and are spread out on the bottom of a large drying oven, which is likewise heated by the vapour from the soffioni. The layer of crystals, which is two or three inches thick, is stirred at intervals to assist the drying. This is complete in twenty-four hours. An improved form of evaporating apparatus consists in decanting the solution in the reservoirs from which the suspended matter has deposited into a pan, and thence running it into a slightly inclined trough made of sheet lead with the edges turned upwards. The trough has an undulatory form, is supported on wooden sleepers, and heated by the soffioni vapours. The solution of boric acid, after passing through this heated trough, becomes so concentrated as to be ready for crystallisation.

Artificial soffioni have been bored to a depth of 200 feet in the vicinity of the Monte Rotondo. The chief works are at Monte Cerboli, Larderello, San Federigo, Castel Nuovo, Sasso, Monte Rotondo, Lustignano, Serranzano, Lago, and San Eduardo, each of which has from 8 to 35 *lagoni*, 100 to 200 feet in diameter (Payen, Ind. Chem. transl. by Paul).

The boric acid thus obtained is far from pure. Analyses of different samples by Payen, Vohl, and Wittstein show that it contains from 74 to 80 p.c. crystallised boric acid, from 4·5 to 7 p.c. of hygroscopic water, ammonium and magnesium sulphates 8–14 p.c., together with gypsum, clay, sand, sulphur, organic matter, and free acids and ammonia.

The origin of the boric acid in the soffioni is not understood. Dumas suggested that it is formed by the decomposition by means of water of a bed of boron sulphide formed at some depth below the surface. Bolley (Annalen, 68, 122) supposed that it is produced by the action of a hot solution of ammonium chloride upon the borates contained in the earth. According to Warington (Chem. Gazette, 1854, 419), Wöhler and Deville (Annalen, 105, 69), and Popp (Annalen, Suppl. 8, 1), its formation is probably due to the action of water upon boron nitride.

Dieulafait has found boric acid in regions where there are no visible manifestations of volcanic action, and concludes that it is of aqueous origin, and derived from the waters of ancient seas (Compt. rend. 100, 1017, and 1240).

Of late years the importation of boracite from South America and colemanite from California, and also some Persian ores, has had a considerable effect on the Italian industry. Besides the obvious method of separating the boric acid from these ores by acidification and

crystallisation, other processes are used for its extraction.

One process consists in grinding the borate of lime or ulexite to an impalpable powder and treating it with sulphurous acid.

A large wrought-iron tank, circular in shape and egg-ended, is lined with stout sheet lead; it is provided with a cover and still head, mechanical agitator, and steam pipes. It is first of all charged about half full with water or weak liquor from a previous operation. The liquor is then boiled, and the powdered borate fed in by means of an Archimedean screw.

Sulphur is then burnt in an adjoining furnace, and the sulphurous gas is injected by means of a peculiarly constructed lead injector into the boiling liquor. A special type of sulphur burner for this process is patented by the American Borax Co. (U.S. Pat. 809550, 1906). The gas is wholly absorbed by the calcium borate, which itself is slightly soluble in water, boric acid and calcium sulphite being formed. The steam arising from the operation, containing boric acid vapours, passes from the still head through a condenser in order to prevent any loss that would occur. When the operation is complete, the steam and gas are shut off, and the contents of the pan allowed to settle, which occupies about ten hours. The clear boric acid liquor is then run either into vats made from white sugar pine, or of ordinary wood lead-lined, where the boric acid crystallises out. The mother liquors are then drawn off, to be used over again if not too highly impregnated with foreign salts, or still further treated for the recovery of the calcium sulphite and the slight percentage of boric acid they contain.

Bigot (J. Soc. Chem. Ind. 1899, 830) obtains it by heating together borate of calcium and ammonium sulphate in a closed vessel. The ammonia driven off is condensed and collected, and the boric acid obtained by extraction of the residue.

Another method is to treat boracite with sodium bisulphate, a by-product in nitric acid manufacture. The two are dissolved in theoretical quantities in water to a density of 15°B. at 100°. The solution is filtered and concentrated to 30°B. On cooling, the boric acid crystallises out and very pure sodium sulphate is obtained by concentration of the mother liquors (Heidlberg, Chem. Zeit. 1907, 31, Rep. 48).

Chenal Douilhet & Co. (D. R. P. 110421, 1899) produce boric acid by taking advantage of the fact that when a borate is boiled with ammonium chloride, ammonia and boric acid are produced. If the concentration is too high, there is a tendency to recombination; the boric acid is therefore removed frequently by crystallisation from portions of the liquid, the mother liquors being returned to the main volume. By this process it is claimed that 98–99 p.c. of the boric acid in combination is recovered.

In another process chlorine is passed into water at 70° containing finely powdered calcium borate in suspension. Calcium chloride and chlorate and boric acid are produced. The boric acid is removed by cooling, and the mother liquors used again until sufficiently concentrated for convenient extraction of the chlorate (G. C. Moore, Eng. Pat. 20384, 1899).

Metallic Borates.

Borates are obtained by the action of boric acid on metallic oxides or their salts, in either the dry or wet way.

In solution boric acid is a very weak acid, being expelled by almost all acids from its combinations, partially so even by carbonic and hydrosulphuric acids. A boiling concentrated solution, however, decomposes carbonates and soluble sulphides and manganese sulphide.

In the dry way, at high temperatures, it is capable of decomposing the salts of all more volatile acids.

Alkaline borates are soluble in water, but are precipitated by alcohol. The remaining borates are insoluble, or very sparingly soluble in water. The soluble borates produce precipitates in solutions of salts of calcium, barium, strontium, nickel, and cobalt, and of ferric salts, which are readily soluble in ammonium chloride.

Anhydrous borates are produced by fusing together, in a special furnace at 1350°–1400° for three hours, boric oxide with the necessary quantity of oxide, carbonate, or nitrate of the metal. With large excess of boric acid, lithium, potassium, sodium, rubidium, cæsium, thallium, and silver produce clear fusions which either crystallise or leave clear glasses on cooling. Cuprous oxide, and oxides of lead, bismuth, antimony, arsenic, titanium, molybdenum, and tungsten produce clear fusions at the high temperatures which form emulsions on cooling. The oxides of calcium, strontium, barium, magnesium, zinc, cadmium, manganese, iron, cobalt, and nickel, do not give homogeneous fusions, but separate into two layers (W. Guertler, J. Soc. Chem. Ind. 1908, 158).

Borates have also been prepared electrolytically by Levi and Castellani by electrolysing boric acid and an alkaline earth chloride in a special type of divided cell (J. Soc. Chem. Ind. 1909, 248).

Ammonium borates. *Laderellite* $(NH_4)_2B_{10}O_{16},5H_2O$ occurs in the Tuscan lagoons in small crystalline rhomboidal plates (D'Achiardi, Chem. Soc. Abstr. 1900, 600). Atterberg (Zeitsch. anorg. Chem. 1906, 48, 367) distinguishes a *diborate* $(NH_4)_2B_4O_7,5H_2O$, crystallising in tetragonal pyramids, besides the *pentaborate*

$$(NH_4)_2O,5B_2O_3,3H_2O,$$

crystallising in rhombic double pyramids previously prepared by Rammelsberg.

Calcium borates $Ca_2B_6O_{11}$. There are three varieties of calcium borate, which correspond to the three varieties of calcium carbonate, calc spar, marble, and chalk—viz. *boracite* or *pandermite*, *colemanite*, and *pricite*—each found in different parts of the world in large quantities, and of a well-defined and constant composition. Meyerhoffer and van 't Hoff (Annalen, 351, 100), in attempting to prepare compounds of similar composition artificially, have obtained several other calcium borates. These authors assign different compositions to colemanite and pandermite. *Boracite*, in outward appearance, closely resembles a snow-white, fine-grained marble; *colemanite* is of a crystalline nature like calc spar, or Iceland spar, and has been termed *borate spar*; *pricite*, or *bechilite*, is a very fine, white,

soft, chalky mineral of a cohesive nature, easily rubbed to powder, and resembling chalk. Chemically speaking, they are all hydrated calcium borates, differing only in their composition in respect to the water of combination, their composition being given in table below.

—	$Ca_2B_6O_{11}$,3Aq.	$Ca_2B_6O_{11}$,4Aq.	$Ca_2B_6O_{11}$,5Aq.	$Ca_2B_6O_{11}$,6Aq.
Boric acid B_2O_3 . . .	55·8	53·3	50·9	48·8
Lime CaO	30·0	28·4	27·2	26·1
Water H_2O	14·2	18·3	21·9	25·1
	100·0	100·0	100·0	100·0

Boracite has been extensively mined at Sultan-Chairi, in the district of the Villayet of Brousa in Asia Minor, forty-five miles from Panderma, a port on the Sea of Marmora; the principal deposits, as far as yet known, exist near the Tschataldga Mountain, in long. 28° 2″ east of Greenwich and lat. 40° north. The Susurlu river runs from the Tschataldga Mountain to the Sea of Marmora; it is partly navigated to a point called Mohalitch; the field is situated in a basin of Tertiary age, surrounded by volcanic rocks, which vary from granite on the east to trachyte on the north, and columnar basalt on the west. Several basaltic hills and dykes protrude in different portions of the basin, and the presence of hot and mineral springs further testifies to the volcanic influences which have been at work, and in which, doubtless, originated the boracic mineral. The latter occurs in a stratum at the bottom of an enormous bed of gypsum; its greater sp.gr. probably impelling it downwards, while the whole mass was yet in a soft state. Several feet of clay cover the gypsum bed, which is here 60 or 70 feet thick, though in places it attains to double that thickness. The borate strata vary in depth, and have been proved for a vertical distance of 45 feet. The mineral exists in closely packed nodules of very irregular size and shape, and of all weights up to a ton. It is easily separated from the dark-coloured gypsum in which it is embedded, and a number of people are employed at the pit mouth in picking and selecting the material. It is sold on a basis of 40 p.c. boric acid, which would be equal to 78·5 p.c. of the pure calcium borate with five molecules of water $Ca_2B_6O_{11}$,5Aq., the remainder consisting of calcium sulphate and other impurities.

Borate spar or *colemanite* has been extensively mined since 1883 at Calico, in San Bernardino county, California, 462 miles south-east of San Francisco. The geological formation of the surrounding hills consists of black lava, sandstones of different colours, gypsum, steatite, and calcium carbonate; it is found in veins and seams from 2 feet to 8 feet in thickness, in some cases dipping at an angle of 36°, and at others running into the hillsides almost horizontally. Its colour and streak is white-milky to transparent; hardness 3·5–4; sp.gr. 2·4; before the blowpipe it exfoliates, decrepitates violently, and melts imperfectly after considerable heating; it imparts a reddish-yellow colour to the flame, which changes to green. The fragments are obscurely rhombic and pulverise easily; it is wholly soluble in hot hydrochloric acid; from the solution boric acid crystallises on cooling. Lustre of the mineral is vitreous to adamantine. The veins and seams are interspersed with masses of calcium carbonate and magnesium silicate, from which, like the boracite, it has to be picked and selected.

Its formula is $Ca_2B_6O_{11}$,5Aq.; it is sold on the basis of 40 p.c. boric acid. Average samples from the bulk vary in composition from 33·8 p.c. boric acid up to 41·2 p.c.; the following analyses may serve as examples of the general composition:—

BORATE SPAR.

Component parts	1	2	3	4	5
*Calcium borate $Ca_2B_6O_{11}$5Aq. . .	66·2	70·4	75·0	78·00	80·80
Calcium carbonate $CaCO_3$ . .	16·3	15·1	11·6	8·75	7·17
Insoluble matter SiO_2 . . .	10·5	10·2	8·9	7·10	7·60
Remaining impurities MgO, &c. .	7·0	4·3	4·5	6·15	4·43
—	100·0	100·0	100·0	100·00	100·00
*= to boric acid	33·8 p.c.	35·9 p.c.	38·2 p.c.	39·8 p.c.	41·2 p.c.

Borate spar is also found in the neighbourhood of Furnace Creek, Inyo county, California; its outward appearance is frequently so exactly like calc spar as often to be mistaken for that mineral. Pricite has hitherto not been so extensively mined as boracite and colemanite; a mine of this mineral, however, exists at Lone Ranch, Cheteo, Curry, county Oregon, from which source, since the first cargo was extracted by E. L. Fleming in 1888, several hundred tons have been taken. It is found embedded in boulders of different size, the nodules varying in weight up to one ton. It is of a soft chalky nature, purely white, can be easily rubbed to powder, but is of a cohesive character; it is very soluble in sulphurous acid, hydrochloric

acid, or acetic acid, yielding boric acid. The following analysis from bulk shows its composition :—

Boric acid B_2O_3	44·24
Lime CaO	30·91
Water H_2O	23·00
Magnesia MgO	0·65
Silica SiO_2	1·20
	100·00

Bechilite is a calcium borate found in the lagoons in Tuscany.

Its composition is represented by the formula $CaB_4O_7,5H_2O$.

Boronatrocalcite. Ulexite, tiza, cottonballs, hayesine $Ca_2B_6O_{11}Na_2B_4O_7,16H_2O$, is a soft, fibrous, silky mineral of a brilliant white when pure, generally found in nodules of a yellowish-white colour, varying in size from that of a Brazil nut to a potato. This curious mineral was first found in the nitre beds of Peru in small quantities, and was examined by Ulex in 1836. It was discovered in Tarapaca, 30 miles from Iquique, under the crust that covers the nitrate of soda beds. It has since been discovered in Chile, Bolivia, California, Nevada, Nova Scotia, and Persia.

Its composition is constant, containing, when pure :

Boric acid B_2O_3	43·1
Lime CaO	13·8
Soda Na_2O	7·7
Water H_2O	35·4
	100·0

The nodules are frequently found incrusted with a coating of sodium sulphate and salt, from which cause the percentage of boric acid in large parcels varies considerably, the average being from 18 to 25 p.c.

Chile has hitherto been the principal source of supply of this borax material. Ulexite, when in a state of fine division, is difficultly soluble in boiling water.

Calcium borosilicate. Dotolite (*Howlite*). A siliceous borate of lime, colour white, streak white, opaque, of a chalky nature, found at Calico, San Bernardino county, California, and at Brookville, Nova Scotia. Composition :

Boric acid B_2O_3	44·22
Lime CaO	28·69
Silica SiO_2	15·25
Water H_2O	11·84
	100·00

Copper borate is readily obtained by treating a soluble borate in solution with copper chloride or sulphate. It is blue, and used in certain oil paints and also in the colouring of porcelain.

Iron borate. A hydrated borate of iron, *lagonite* $Fe_2O_3,3B_2O_3,3H_2O$, is found in the Tuscan lagoons.

Lead borates. By mixing concentrated solutions of lead nitrate and borax, the metaborate $Pb(BO_2)_2,H_2O$ is precipitated, and by the use of solutions of smaller concentrations Rose obtained many basic salts. They all melt on strong heating to colourless or light-yellow, highly refractive glasses, the hardness increasing with the boron content. Glasses may be obtained by fusing together lead oxide and boric acid in any proportions greater than 0·0725 equivalent of PbO to 1 equivalent B_2O_3, but below this limit an emulsion is formed on cooling.

Magnesium borates. *Stassfurtite* (*Szaibelyte*). This mineral occurs crystalline and massive, colour white, streak white, fracture conchoidal uneven, subtransparent, translucent, lustre vitreous inclining to adamantine, hardness 7, sp.gr. 2·83, pyro-electric, soluble in acids. It is found at Stassfurt, Prussia, embedded in the kainite beds, the composition being :

Boric acid B_2O_3	62·33
Magnesia MgO	27·03
Chlorine Cl	7·91
Magnesium Mg	2·73
	100·00

It is also found in nodules in grey limestone at Werksthal, Hungary, and at Danbury, Connecticut, United States.

Sussexite is a hydrated borate of manganese and magnesia found in Sussex county, New Jersey, United States. *Tourmaline*, found in different parts of the world in different colours, also contains a small percentage of boric acid.

Potassium borates. Atterberg distinguishes five different potassium borates : a monoborate $K_2O,B_2O_3,3H_2O$; three diborates $K_2O,2B_2O_3$ crystallising with 4, 5½, and 6 molecules of water respectively ; and Laurent's pentaborate $K_2O,5B_2O_3,8H_2O$ (Zeitsch. anorg. Chem. 1906, 367).

Sodium borates. The only commercially important compounds are sodium diborate (*v. Borax*) and the perborate (*v. Perborates*). The metaborate $NaBO_2,4H_2O$ is readily obtained by fusing together the necessary proportions of boric acid and sodium carbonate, and crystallising.

Sodium diborate, or *Borax*. Borax occurs in the crude state in what are termed borax marshes, which are generally the bottoms of dried-up lakes, or, where tincal is found, lakes that are nearly dried. The crude borax in the former instances is found lying on the surface of the plain, of a peculiar greyish-yellow colour, having a depth of from 1 inch to 18 inches. It is generally associated with other substances, both soluble and insoluble, as the table of analyses (p. 505) shows.

At Jagadhri in Northern India, 37 miles S.E. of Umballa, there is a borax refinery, the product of which is shipped to Calcutta. The quantity of tincal and borax obtained from the districts of the Himalayan Mountains amounts to about 2000 tons per annum. The tincal deposits are of very ancient origin. In North America there are no less than ten deposits, five of them being in the State of California—at Saline Valley, Furnace Creek, and Armagora (in Inyo county), Slate Range (in San Bernardino county), and Lower Lake (in Lake county) ; the remaining five are in the State of Nevada—at Rhodes, Teels Marsh, Columbus, and Fish Lake (in Esmeralda county), and Salt Wells (Carson Lake, Churchill county).

Borax was first accidentally discovered in California, in 1856, by Dr. John A. Veatch, since which time the different deposits mentioned have been developed, and the available supply

COMPOSITION OF CRUDE BORAX FROM THE MARSHES.

—	1	2	3	4	5	6	7	8
Sodium biborate	30·30	38·3	2·10	53·08	1·9	33·30	6·52	45·20
Water	37·68	40·8	14·08	39·24	25·7	25·88	16·46	43·80
Sand and insoluble matter	18·00	10·9	12·80	1·20	33·0	2·40	8·80	7·15
Sodium carbonate	6·10	5·3	16·10	5·50	34·3	13·70	18·30	2·75
Sodium sulphate	0·26	0·1	19·10	0·35	0·5	8·25	20·22	—
Sodium chloride	0·50	0·4	34·60	0·50	0·7	15·40	28·20	0·40
Calcium carbonate	3·28	2·4	0·70	—	2·0	0·60	0·80	0·30
Magnesium carbonate	2·26	0·4	0·30	—	0·6	0·30	0·50	0·30
Oxide of iron and alumina	1·62	1·4	0·22	0·13	1·3	0·17	0·20	0·10
	100·00	100·0	100·00	100·00	100·0	100·00	100·00	100·00

is practically unlimited, and is solely regulated by the demand. The exports of borax from America have increased very greatly of late years, and, to a large extent, have taken the place of the Italian product.

Commercially, borax is valued by evaporating to dryness a known weight of the sample with hydrochloric acid, and estimating the chloride volumetrically in the residue with silver nitrate. Any chloride present in the sample as impurity is estimated separately and allowed for, the percentage of borax being calculated from the equation

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3.$$

Properties.—Borax forms two varieties of crystals, (1) the *decahydrate*, which is produced by allowing solutions of borax to crystallise by cooling down to the ordinary temperature; (2) *octahedral borax*, which is a pentahydrate which separates out when the solution is allowed to crystallise above 50°.

1. *Ordinary or prismatic borax* $Na_2B_4O_7$, $10H_2O$ forms large transparent monoclinic prisms with truncated lateral edges. They effloresce when exposed to the air, have a rather sweet cooling alkaline taste, and a sp.gr. of 1·75. When heated they melt in their water of crystallisation, swell up, and leave a porous spongy mass, called burnt or calcined borax (*borax usta*), and fuse at a red heat to a colourless anhydrous glass (vitrified borax) with a sp.gr. of 2·36, which gradually absorbs water from the air, reforming prismatic borax. At 62° the decahydrate undergoes transition into the pentahydrate.

When borax is distilled with methyl alcohol, about 50 p.c. of the boric acid comes over fairly readily, and on longer treatment nearly 60 p.c. From the liquor remaining in the flask, crystals of $NaBO_2,5CH_3OH$ separate (Polenske, Analyst, 1902, 34).

Borax dissolves in water, but is insoluble in alcohol. The aqueous solution has an alkaline reaction, and changes the colour of an alcoholic solution of turmeric to brown; a small quantity of a mineral acid restores the original yellow colour, but a larger quantity liberates boric acid in sufficient quantity to produce the characteristic brown colouration. The following determinations of its solubility are those of Horn and van Wagener (Amer. Chem. J. 1903, 346):—

$t°$	100 grams H_2O dissolve of anhydrous borax $Na_2B_4O_7$	$t°$	100 grams H_2O dissolve of anhydrous borax $Na_2B_4O_7$
5°	1·3 gram	60°	19·9 grams
21·5°	2·8	70°	24·4
30°	3·9	80°	31·4
45°	8·1	90°	40·8
50°	10·5	100°	52·3
55°	14·2		

At the temperature of 27°, borax solutions hold 1 lb. of borax to the imperial gallon, and have a sp.gr. of 1·050, or 10°Tw. The general crystallising strength is 1·160 sp.gr., or 32°Tw., when the solution holds 5 lbs. of borax to the gallon, crystallisation commencing at 65·5°.

Borax is easily decomposed by acids. *Hydrochloric acid* leaves, on evaporation, sodium chloride and free boric acid. *Carbonic acid* is absorbed by a solution of borax from the air, and no borax is precipitated on the addition of alcohol. Saturated with *sulphuretted hydrogen* and mixed with alcohol, the liquid separates on the addition of ether into two layers, the lower containing sodium sulphide, the upper free boric acid.

It forms double salts with arsenious acid of the empirical formula

$$3Na_2O{\cdot}6B_2O_3{\cdot}5As_2O_3+10Aq.$$

(Schweizer, J. 1850, 257). With *sodium fluoride* it forms sodium fluoborate. When 1 pt. tartaric acid is mixed with 2 pts. of a hot solution of borax, boric acid separates out on cooling. If the tartaric acid be increased, the separation of boric acid likewise increases up to a certain point, after which it diminishes, and ultimately is no longer separated. *Acid tartrate of potassium* forms a double salt with borax. *Silicic acid* is insoluble, or nearly so, in solutions of borax.

Benzoic, tartaric, and gallic acids dissolve more readily in borax than in water. Many fatty acids and resins dissolve as readily in borax as in alkaline leys, the borax behaving like a mixture of boric acid and free soda.

At a red heat, however, the boric acid in borax readily dissolves and unites with metallic oxides, forming a fusible glass of a double salt, which property renders it of great use in soldering and in metallurgical operations and in blowpipe analysis, the glasses thus formed often exhibiting characteristic colours. It is used also in the preparation of easily fusible glass fluxes for enamels and glazes.

2. *Octahedral borax* $Na_2B_4O_7,5H_2O$ is obtained by allowing a saturated solution of borax to cool down to about 60° in a warm place and removing the crystals.

The crystals are regular, transparent octahedra, harder than the ordinary borax. They have a conchoidal fracture and a sp.gr. of 1·8. They do not change in dry air, but absorb moisture very readily and become prismatic. They fuse more readily than the prismatic crystals, and with less intumescence, and without splitting. Octahedral borax is therefore better adapted for soldering and as a flux than common borax, and the smaller quantity of water (a difference of 17 p.c.) diminishes the cost of transport. The prismatic variety is, however, generally preferred, probably because it is cheaper weight for weight.

The commonest impurities in borax are sodium carbonate and small quantities of chlorides and sulphates of sodium, calcium, and magnesium. It is occasionally adulterated with earthy matters, alum, and sodium chloride. It should dissolve in two parts of boiling water and should not effervesce with acids. The aqueous solution should not be rendered turbid when treated with an alkali, or with barium chloride or silver nitrate in presence of nitric acid.

The manufacture of borax from boric acid.

This industry is chiefly associated with the production from the Tuscan lagoons. The crude acid, packed in large casks weighing about 13 cwts., on arrival at the borax works is first of all manipulated in the casks themselves. For this purpose, the cask is placed on what is termed a stillage, the head taken off, the acid loosened with a spade and treated with small quantities of water for the purpose of washing out the sulphates of ammonia and magnesia, which, on account of their greater solubility, easily separate from the less soluble boric acid, the washings being used for the recovery of the ammonia and magnesia they contain, whilst the acid, which formerly contained 83·46 p.c. $B_2O_3 3Aq.$ or equivalent to 128·5 p.c. borax, is brought up to a strength of 96·67 p.c. $B_2O_3 3Aq.$ or equivalent to 148·87 p.c. borax. The acid, after draining for twenty-four hours, is then placed in wicker baskets and transferred to the saturators. These are made of wrought-iron $\frac{3}{8}$ plates, having a diameter of 10 feet, egg-ended, height 9 feet 6 inches, provided with hopper and swivel discharge, still head, inspection glasses, run-off stop-cocks, and connected by steam pipes with a perforated iron coil in the bottom of the pan for the purpose of boiling the borax liquor with injected steam. There is also a manhole with movable cover. When the saturator is ready for charging, liquor is pumped in to the height of 4 feet, or 2300 gallons, which is then boiled with steam and soda ash. Anhydrous sodium carbonate is then added, about 23 cwts. being generally required to 60 cwts. of acid. When the soda ash is all dissolved, the manhole lid is placed on, and the boric acid is put in by degrees through a hopper, half a hundredweight at a time. At each addition of acid a brisk ebullition of carbonic acid takes place, which passes along the still head, and after being deprived of its ammonia may be utilised for making bicarbonate of soda.

After the saturator has received its charge of soda ash and acid, the liquor is thoroughly boiled for five hours and allowed to settle, in order that the solid impurities may subside. This generally occupies from eight to ten hours, after which the liquor is run into large wrought-iron vats 12 feet long, 6 feet wide, 4 feet deep, into which the wires made of iron, technically called 'straps,' are suspended over bars of wood laid across the top of the vat. The liquor on cooling crystallises on the wires, sides, and bottom of the vat, and when the temperature has fallen to 26° (80°F.), the liquor is siphoned off from the vats, and men get in, and, by the aid of iron bars terminating in a chiselled end, first remove the crystallised borax from the straps, then cut up the borax crystallising on the bottom of the vat, and lastly knock down the sides. This borax is not of sufficient purity for the market, and is, therefore, subjected to a second refining, and, if necessary, bleaching. For this purpose a series of pans, called refining pans, are employed; they are also of wrought iron, circular, 9 feet diameter, egg-ended, 8 feet deep, open at the top and provided with cradles of wrought iron perforated with holes, suspended by iron chains from a patent block overhead in such a manner as to be raised or lowered in the pans as required. The pans are boiled with steam issuing from a perforated pipe in the bottom. They are first half filled with water, or some of the clearest liquor from a previous operation, and when the liquor is boiling crude borax is thrown into the cradle and allowed to dissolve. The right amount of borax is tested by means of the Twaddell hydrometer, which should read 30° when the liquor is of the required strength. About 5 cwts. of sodium carbonate is added, and a little chloride of lime, and the whole thoroughly boiled. The saturated liquor is then allowed to settle in the pans for ten hours, covers being placed on them to prevent the liquor chilling; the pans are run off into vats of similar size and shape to those employed in the first process, and the borax allowed to crystallise, which takes six days. Upon the expiration of that time, the liquor is siphoned off to a well, made by sinking a wrought-iron tank in the ground below the level of the vats, and, if impure, is pumped up to the refining pans to be used over again, and if sufficiently pure is pumped to boiling-down pans, to be concentrated to such a degree as to yield a further crop of borax.

The liquors from the first vats are also pumped to the boiling-down pans, where they likewise undergo a process of concentration. These boiling-down pans are made of wrought iron, and are capable of holding about 4000 gallons. They are provided with dry-steam coils, and are superior to other means of concentration from the fact that they are completely under control, and the evaporation of the liquor can be regulated as fast or as slow as may be necessary. The liquors in these pans are concentrated until they reach a sp.gr. of 1·300, or 60° Tw., when they are run off into vats to yield first a crop of borax, and then upon reaching a temperature of 80°F. they are siphoned off into other vats, where they yield a crop of Glauber salts, or sodium sulphate, after which the liquors, being rich in sodium carbonate, are used again in the saturators for making up a fresh batch of

borax with acid and soda ash. The mother liquors, strong in common salt and weak in sodium carbonate, are further concentrated in jacketed pans, where, on continued boiling, the salt falls to the bottom, is collected by means of rakes, and fished out with perforated scoops provided with long wooden handles, and the salt is ladled into iron baskets set over the pans and allowed to drain. By this means all the salts contained in the soda ash and boric acid are saved, and nothing is run to waste.

The washings from the boric acid in the first process, containing the ammonium sulphate and magnesium sulphate, are collected together, and placed in a wrought-iron still provided with a dry-steam coil. The requisite amount of sodium carbonate is then added, and the ammonium carbonate is distilled off, yielding a highly concentrated and very pure carbonate of ammonia liquor, which is either sold in that state or utilised for making the purest volcanic ammonia salts.

The borax from the refined vats, consisting of the straps and sides, is carried to the packing room, there to be picked, selected, and packed in casks, whilst the borax bottoms, not being in the form of merchantable borax, are refined again.

Manufacture of borax from borate of lime.

The mineral is first crushed in a stone breaker, the size of jaws being 8 inches and known as No. 4, easily capable of crushing 12 tons in twenty-four hours. As the mineral passes through it is taken up by an elevator and run through millstones, 30 inches in diameter, and placed by the side of the crusher. There are two pairs, one grinding fresh ore and the other grinding the tailings. The millstones deliver the powdered ore into another elevator, which passes it through a bolting or sifting machine, 10 feet long and 30 inches in diameter, having octagonal sides, the bolting cloth being of silk known as No. 8. As considerable fine and impalpable dust arises from the sifting, it is kept down by means of an exhaust fan blowing the dust into a dust room. The fine mineral is conveyed by means of an Archimedean screw and elevator into bins, each holding a certain quantity and placed over the saturators. These are wrought-iron tanks capable of holding a charge of 2500 gallons, and provided with suitable agitators and either dry or wet steam coils, the bottom of the saturators being connected by 3-inch wrought-iron valves and pipes to a powerful pump for the purpose of removing the contents of the saturator when desired. The saturators are grouped together in sets of four for facilitating the lixiviation of the contents by means of repeated washings, after the first decomposition of the mineral. The saturators, as in the case of the manufacture of borax from boric acid, are first charged with liquor and brought to the boil; a charge of soda ash, usually about 30 cwts., being put in, which is sufficient to decompose three tons of the borate of lime which is gradually added after the soda ash is all dissolved. The soda ash gradually but completely decomposes the sesquiborate forming calcium carbonate, borate of soda, and biborate of soda:

$$Ca_2B_6O_{11}+2Na_2CO_3 = 2CaCO_3+Na_2B_4O_7+2NaBO_2.$$

After *boiling five hours the steam* and agitators are stopped, and the muddy liquor allowed to settle for ten hours, after which time the clear supernatant liquor is run off to vats to crystallise, and the residue is again washed with weaker liquor from the saturator previously washed, the operation being repeated of boiling and washing with the gradually weaker liquors from the other saturators in rotation. By the time the mud has received eight washings, the last being with water, the whole of the borax will have been removed, and the chalk which is left is then pumped through an iron filter press, which completely presses out the remaining weak liquor and leaves the chalk in a solid cake, which is generally thrown to one side, being too impure for any purpose. The first liquor run to the vats contains the biborate and borate of soda, together with carbonate and sulphate of soda in solution. The biborate of soda or borax crystallises out after cooling in the vats for about six days, leaving the borate of soda in solution. The liquor is then siphoned off into the well and pumped to the boiling-down pans, where it undergoes the process of concentration until it reaches a sp.gr. of 1·350 to 1·400 (70° to 80°Tw.), when it is run off into vats and allowed to throw a further crop of borax. The mother liquor is now of a syrupy consistence, and is pumped into a decomposing tank, where carbon dioxide is blown through it. The following decomposition takes place:—

$$4NaBO_2+CO_2=Na_2B_4O_7+Na_2CO_3.$$

The borax falls to the bottom of the tank in a finely divided state, whilst the sodium carbonate remains in solution, and can be used over again in the saturators for the first operation. The refining of the borax from the first process is the same as that employed in the boric acid process, and therefore need not be further described. The only precaution necessary is the addition of a little bicarbonate of soda in the pans to decompose any borate of soda that might be associated with the borax. Three tons of borate of lime produce 2 tons of borax and 1 ton of borax in the state of metaborate of soda. Metaborate of soda may be formed by mixing the concentrated solutions of borax and caustic soda together in their equivalent quantities, and evaporating to 70°Tw.:

$$Na_2B_4O_7+2NaHO=4NaBO_2+H_2O$$

from which the metaborate of soda crystallises in needle-shaped crystals having the formula $NaBO_2,4H_2O$.

100 parts of metaborate of soda, when decomposed by carbonic acid, produce 65·6 parts of borax and 34·4 parts of sodium carbonate; about 30 cwts. of borate of soda thus produce 20 cwts. of borax.

The following process is used by Masson, Gembloux, and Tillière, Brussels. An ammonium salt is treated with lime in a distilling column and the ammonia set free is passed into water contained in a digester, and the digester is then charged with carbonic or sulphurous acid. The digester is gently heated and pandermite is introduced. It is then closed and more strongly heated for several hours, whilst the contents are mechanically agitated and are transferred, when the action is complete, to filter presses, whence the liquor passes to a reaction chamber where it

is agitated with sodium chloride and, after addition of a little ammonia, is discharged into crystallisers. After removal of the borax which crystallises out, the mother liquor is used instead of water in the succeeding operation. After several operations, the mother liquor requires a special treatment.

In this process, an ammonium biborate is first obtained by the ammonium carbonate treatment of calcium borate, and from this ammonium salt borax is obtained by double decomposition with sodium chloride. Boronatrocalcite may be used instead of pandermite if the process is slightly modified.

Manufacture of borax from ulexite.

Borax is manufactured from this mineral at the various deposits, and also in England, France, and Germany, to which places it is exported from Chile and California, selected and packed in sacks.

The first operation consists in reducing the material to a state of fine division, and for this purpose a mill is used so constructed as to tear the borate to pieces instead of grinding it, which, owing to its fibrous silky nature, is found preferable.

The borate is then mixed with its proper proportion of soda ash and bicarbonate of soda, or soda ash and boric acid, having regard to the fact that, if associated with much gypsum, a proportionate additional allowance of soda ash must be made, as the gypsum decomposes the sodium carbonate, forming sodium sulphate and chalk. The composition of ulexite being $Ca_2B_6O_{11}{\cdot}Na_2B_4O_7$, it requires one equivalent of bicarbonate of soda and one equivalent of carbonate of soda to decompose it:

$$2(Ca_2B_6O_{11}Na_2B_4O_7)+2NaHCO_3+2Na_2CO_3 = 5Na_2B_4O_7+4CaCO_3+H_2O.$$

These ingredients are all mixed together in the dry state. The process adopted is similar to the processes already described—namely, that of first boiling the liquor in the saturator, then gradually adding the crude material, boiling, settling, lixiviating.

100 parts of the ulexite, testing 43 p.c. boric acid, require 10 parts of bicarbonate of soda and 12 parts of carbonate of soda, for its conversion into 117 parts of borax.

Manufacture of borax from crude borax.

This branch of the industry is generally carried on at the borax marsh. It may be desirable to give a description of the Saline Valley, Inyo county, California, where the most extensive deposit of natural borax exists in North America, before entering into the details of refining.

The valley, situated on the eastern slope of the Sierra Nevada Mountains, 11 miles from the Carson and Colorado railroad, is 18 miles long and 12 miles wide, surrounded with mountainous hills which afford no outlet, and therefore the valley may be said to be the bottom of a dried-up lake. At the point of deepest depression an area of over 1000 acres is covered with crude borax from 6 to 18 inches in depth. The colour of the crude material as it lies upon the level plain is a peculiar grey yellow. The borax in Saline Valley is mixed with sand, which is volcanic ash and decomposed lime rock, sodium sulphate, sodium carbonate, and sodium chloride. The surrounding hills consist of granite, marble, dolomite, black lava, and felspar. The composition of the crude material varies in strength from 10 p.c. of borax up to 90 p.c., whilst in some places on the marsh—under a crust composed of sodium sulphate, sodium carbonate, and common salt—beds of tincal, or large crystals of borax, some two feet in thickness, are found; whilst below the tincal there is a strong saturated yellowish liquor containing 1 lb. of borax to the gallon. All the manipulation that is required is to shovel off the surface of the marsh to a depth of 18 inches and cart the material to long hemispherical wrought-iron pans set on arches of stone, fired beneath with wood fuel obtained in the neighbourhood. The pans are charged with water, and the crude material thrown in and vigorously stirred with long poles, until, with the aid of heat, all the soluble salts are dissolved. The fires are then withdrawn, and the contents of the pans allowed to settle for ten hours, when the liquor is drawn off into vats, where the borax crystallises out. The mother liquor after six days is drawn off, and the borax is taken out and packed into sacks for shipment.

Borax and boric acid are applied in the manufacturing industries as follows:—

Brick and tile makers. Glazed surfaces.
Candle makers. Preparation of wicks.
Cement. Making the finest kinds, which take a polish.
China and earthenware. In preparing a frit used for glazing what is technically termed 'biscuit ware' in pottery of all descriptions.
Colour makers. In preparing Guignet's green and borate of manganese (a drier).
Coppersmiths. In brazing.
Druggists. Pharmaceutical preparations.
Enamelled iron. An enamelled coating to cast and wrought iron.
Glass. Making pastes and as an ingredient.
Hat makers. Dissolving shellac for a stiffener.
Ironsmiths. In welding.
Jewellers. In soldering. (Ancient name for borax, 'chrysocolla,' gold-glue.)
Laundresses. As a starch-glaze for linen.
Paper makers. Superfine note and highly glazed paper and cards.
Pork packers. Curing and preserving hams and bacon.
Safe makers. Lining safes to resist fire.
Soap makers. As an emollient.
Tanners. Dressing leather.
Textile manufacturers. Solvent-bleach; mordant; fireproofer.
Timber merchants. In preparation of hard from soft wood.

Perborates are salts of the acid HBO_3 which has not been prepared in the free state on account of its instability. The alkali and alkaline earth salts are soluble in water and have an alkaline reaction. They behave in solution like mixtures of borates with hydrogen peroxide; the active oxygen being liberated by heat, by acidifying the solution, or by large dilution. Oxyclases, reductases, and manganese dioxide cause them to give up the whole of their reactive oxygen. They convert chromic acid and molybdates into perchromic acid and yellow permolybdates. They readily oxidise protoxides and their salts into higher oxides, but do not always form perborates with them. Ferrous, mercurous,

manganous, and lead salts yield higher oxides; the salts of other metals yield perborates of an indefinite or basic composition. Perborates of the alkali metals may be obtained by careful precipitation of solutions of alkali borates with alcohol in the presence of hydrogen peroxide.

Ammonium perborate NH_4BO_3,H_2O is the best characterised of the several perborates resulting from the action of ammonia and hydrogen peroxide on ammonium borate. It contains 16·84 p.c. of active oxygen.

Potassium biperborate $KB_2O_5,2H_2O$ is obtained by the action of hydrogen peroxide on potassium borate.

Sodium perborate $NaBO_3,4H_2O$. When 248 grams of boric acid are mixed with 78 grams of sodium peroxide and added gradually to 2 litres of cold water, the mixture dissolves at first, but later a crystalline substance separates out which may be filtered off and dried. This substance, which has a composition $Na_2B_4O_8$, $10H_2O$, is called '*perborax*,' and is soluble in water to the extent of 42 grams per litre at 11°. When one-half of its sodium is displaced by a mineral acid, a crystalline precipitate of *sodium perborate* $NaBO_3,4H_2O$ separates out. This is a very stable substance, and can be preserved indefinitely at ordinary temperatures. It dissolves readily with slight decomposition in water at 50°–60°, and a vigorous ebullition of oxygen takes place at 100°. The cold aqueous solution possesses all the properties of hydrogen peroxide. When powdered sodium perborate is added gradually to 50 p.c. sulphuric acid, and the solution filtered through guncotton a very strong (150–200 vols.) solution of hydrogen peroxide is obtained.

Patents for the manufacture of zinc and magnesium perborates have been taken out by G. W. Johnson (Eng. Pat. 26790, 1904).

Organic Derivatives of Boric Acid.

Aniline borate, and compounds of *piperidine*, *coniine*, *tetrahydroquinoline*, and *tetramethylammonium hydroxide*, have been prepared by L. & T. Spiegel (J. Soc. Chem. Ind. 1905, 103). The *menthyl* and *bornyl* esters are readily prepared by heating menthol and borneol with boric acid, xylene being used as a medium in the latter case (Verein Chininfabriken, Zimmer & Co., Eng. Pat. 11574, 1906).

Ethyl borosalicylate, or '*boryl*,' is prepared by boiling together 62 grams of boric acid and 138 grams of salicylic acid with 200 c.c. of water. The resulting borosalicylic acid is esterified by adding 60 grams of 95 p.c. alcohol and heating with 40 grams of sulphuric acid. It forms needle-shaped crystals which are more convenient than oil of winter-green for many medicinal purposes.

Zinc boropicrate, or '*chrysyl*,' is the product obtained by boiling together boric and picric acids, and saturating the mixture with zinc oxide. It is a yellow powder used as a medicinal antiseptic (Monteil, J. Soc. Chem. Ind. 1908, 354).

Phenyl borate $B(OPh)_3$, *diphenylboric acid* $B(OH)(OPh)_2$, *m-tolyl borate* $B(OC_6H_4Me)_3$, and *β-naphthyl borate* $B(C_{10}H_7O)_3$, together with several other aryl halogen boron compounds and *p-borobenzoic acid* $CO_2H{\cdot}C_6H_4{\cdot}B(OH)_2$, have been prepared by Michaelis (Annalen, 315, 19–43).

Borcitrates are valuable as remedies in cases of kidney disease and urinary calculi. Their solvent power for urates and phosphates is greater than that of lithium benzoate. The diborocitrates are best adapted for the purpose. The following are known :—

Magnesium triborocitrate $(C_6H_5O_7)_2Mg_3(B_3H_3O_6)_2$
" diborocitrate $(C_6H_5O_7)_2Mg_2(B_2H_2O_4)_2$
" monoborocitrate $(C_6H_5O_7)_2Mg(BHO_2)$

Lithium, potassium, sodium, and ammonium, mono-, di-, and tri-borocitrates of similar constitution have been prepared. Iron salts have also been obtained containing respectively 8 and 16 p.c. of iron by acting on sodium di- and mono-borocitrate with ferric hydrate (Scheile, Pharm. J. [3] 11, 389).

The magnesium compounds possess strong antiseptic properties.

Detection and Estimation of Boron.

Boron almost always occurs in the form of boric acid. When the acid is in the free state it can readily be recognised by the green colour which it gives to the flame, and by its action upon turmeric.

Turmeric paper, when moistened with a solution of boric acid and dried, acquires a cherry-red colour, which is changed to olive-green on moistening with an alkali. Acid solutions of zirconic, tantalic, niobic, and molybdic acids also colour turmeric brown. Cassal and Gerrans (Chem. News, 1903, 27) find that the sensitiveness is greatly increased by the addition of oxalic acid, and base a colorimetric method of estimation of boric acid on this reaction.

The green colour imparted to flame is a very delicate test for boron (according to Merz, J. pr. Chem. 80, 487, 1 part in 1400 may be detected by means of it). It is, however, to be noted that salts of copper likewise colour flame green, as well as certain compounds of chlorine and barium and thallium. When the boric acid is combined with a base the compound in the state of powder is decomposed by means of sulphuric acid, and the boric acid extracted by alcohol. Compounds not decomposed by sulphuric acid are fused with potash and digested with alcohol and sulphuric acid.

The presence of boron in minerals may be detected by mixing the mineral in powder with a flux containing 1 part fluor-spar to 4½ parts hydrogen potassium sulphate, made into a paste with water, and heating the mixture in the inner blowpipe flame, when boron chloride is given off which tinges the flame green; or by mixing the suspected substance with fluor-spar moistening with concentrated sulphuric acid, and passing the escaping gas through a tube drawn to a fine point into the non-luminous bunsen flame, which it colours green.

The spectrum of boron shows three bright lines in the green and one in the blue. Hartley finds in the spectra of boric acid and borax the lines λ3450·3, λ2497, and λ2496·3, which he considers characteristic of boron (Roy. Soc. Proc. 35, 301). (For the measurement of the intensity of these bands, *v.* Lecoq de Boisbaudran, Compt. rend. 76, 883.)

The quantitative estimation of boron is difficult, as all borates are soluble to some extent in water and alcohol, and boric acid

cannot be heated without loss in contact with water.

One method of direct determination is to precipitate the boron as potassium borofluoride, which is quite insoluble in alcohol (Berzelius, Lehrbuch, 3 ed. 10, 84; Stromeyer, Annalen, 100, 82; Thaddeeff, J. Soc. Chem. Ind. 1898, 953). This method has been adversely criticised by Gooch and others, and has been almost entirely superseded.

The most trustworthy method of estimating boron is due to Gooch. If the boron is not present as boric acid, it is brought into that state by heating for some hours in a sealed tube with nitric acid. The resulting solution is repeatedly distilled with methyl alcohol, the boric acid passing over in the vapour. The distillate is then treated with an exactly weighed excess of pure lime, transferred to a platinum crucible, evaporated to dryness on the water-bath and strongly heated. The increase in weight represents the boric anhydride.

Volumetrically, boric acid may be estimated accurately by titration with caustic soda, using phenolphthalein as indicator, if about one-third of the bulk of the solution of glycerol is added (Thomson, J. Soc. Chem. Ind. 1894, 432; *v.* also ANALYSIS).

Boron may be estimated indirectly by digesting a weighed quantity of the finely divided compound in a platinum vessel with hydrofluoric acid, and then with concentrated sulphuric acid. On warming gently, the boron present is expelled as fluoride, and after driving off the excess of sulphuric acid, the quantity of bases in the residue is determined. Their weight, deducted from the weight of the original substance, gives the quantity of boric anhydride.

When combined with potash or soda, boric acid may be determined by evaporating the solution of the previously weighed salt with hydrochloric acid, and determining the chlorine in the dry residue (Schweizer, Pharm. Centr. 1850, 372; J. 1850, 590).

Crude boric acid (Italian) is usually valued by determining the water and the substances insoluble in alcohol, and taking the rest as being boric acid. According to Zschimmer (Chem. Zentr. 1901, [5] 44, and [7] 67), the results are inaccurate, on account of the water not being completely driven off under the conditions used (2 hours drying at 45° and 2 hours in desiccator).

Boron is best estimated in the presence of silicates; *e.g.* in tourmaline, by the method of G. W. Sargent, who has submitted all the processes published to examination and criticism (J. Amer. Chem. Soc. 1899, 858–888). The mineral is fused with alkali carbonates, and, after lixiviating and acidifying, the boric acid is volatilised from the solution as the methyl ester. A convenient form of apparatus for performing this operation is described. The boric ester is subsequently hydrolysed by a weighed quantity of pure lime, and estimated by Gooch's process.

A method for its estimation in insoluble silicates is also given by Wherry and Chapin (J. Amer. Chem. Soc. 1908, 1687–1701).

A solution of boric acid produces no change of colour in solutions of helianthin, tropæolin, and methyl orange, but a drop of hydrochloric acid immediately changes the yellow colour into red. Borax may thus be titrated by the stronger acids (A. Joly, Compt. rend. 100, 103).

(For the estimation of boric acid in mineral waters, *v.* Fresenius, Zeitsch. anal. Chem. 25, 202.)

To detect boric acid in milk, baryta is added to 100 c.c. of milk till alkaline. After incineration, the ash is dissolved in a little strong hydrochloric acid, evaporated to dryness, and a solution of turmeric with a drop of dilute hydrochloric acid added, and the solution evaporated on a water-bath. 0·001 p.c. boric acid gives a distinct colour to turmeric in this manner (J. Soc. Chem. Ind. 1887, 563).

Boric acid may be rapidly determined in butter by stirring a weighed quantity with a known volume of warm standard sulphuric acid till melted, allowing to settle, and titrating a portion of the aqueous part with caustic soda, using phenolphthalein. The pink colour appears when the sulphuric acid has been neutralised; glycerol is then added and caustic soda run in till the colour reappears. The second titration represents the boric acid (Richmond and Harrison, Analyst, 1902, 179).

BORONATROCALCITE. An early name (G. L. Ulex, 1849) for the mineral ulexite, a hydrated borate of sodium and calcium $NaCaB_5O_9,8H_2O$. Most of the natural borates exported from South America (Chili, Bolivia, and Argentina) are of this species: it is also abundant in the borate deposits of California and Nevada. L. J. S.

BOROVERTIN *v.* SYNTHETIC DRUGS.

BORYL. Trade name for ethyl borosalicylate. Prepared by boiling together solutions of boric acid and salicylic acid and esterifying by the addition of alcohol and sulphuric acid. Needle-shaped crystals. Used in medicine as a substitute for ethyl salicylate (Monteil, J. Soc. Chem. Ind. 1908, 354).

BOSCH. An inferior butter prepared in Holland. The term is sometimes used as synonymous with margarine (*q.v.*).

BOSTONITE. A trade-name formerly in use for the Canadian serpentine-asbestos (*v.* ASBESTOS). L. J. S.

BOSWELLIA SERRATA (Roxb.) or **GUGAL.** The gum of this plant (ord. *Burseraceæ*) is used as an incense. It is often confounded with bdellium and olibanum (Dymock, Pharm. J. [3] 7, 190).

BOTANY BAY RESIN *v.* BALSAMS.

BOTRYOLITE *v.* CALCIUM.

BOTTLE-NOSE OIL. An oil obtained from the bottle-nosed whale, closely resembling sperm oil; its sp.gr. varies from 0·876 to 0·880 (Allen, J. Soc. Chem. Ind. 2, 53).

BOUILLON NOIR. *Ferric acetate* (*v.* ACETIC ACID).

BOU-NEFA. The root bark of *Thapsia garganica* (Linn.), an umbelliferous plant growing in the South of Europe and Algeria. It contains a resin used as a medicine in France.

BOURNEENE or **VALERENE.** A liquid hydrocarbon isomeric with oil of turpentine, secreted by the *Dryobalanops aromatica* (Gaertr.), and holding in solution borneol or Borneo camphor. According to Wallach (Annalen, 230, 225; Chem. Soc. Trans. [2] 50, 70), it is a mixture of the decomposition products of camphene.

BOURNONITE. Sulphantimonate of copper and lead $CuPbSbS_3$, crystallising in tabular

orthorhombic crystals; these are frequently twinned and show re-entrant angles at the edges, hence the names 'cogwheel-ore' and 'wheel-ore.' It is found in Cornwall, Harz, &c.; and in Bolivia. It sometimes occurs in sufficient abundance to be used as an ore of copper and lead. L. J. S.

BOVEY COAL *v.* FUEL.

BRAGA. An alcoholic beverage used in Roumania, prepared by the fermentation of millet. The seed is boiled with about 12 times its weight of water for 14 hours, the resulting viscous mass cooled, stirred with water and allowed to ferment. The liquid is filtered and mixed with water, when it is ready for sale. It is somewhat sweet, and contains about 1·3 p.c. of alcohol by weight.

BRAM'S POWDER. An explosive consisting of 60 parts of a mixture of potassium chlorate, potassium nitrate, wood charcoal, and oak sawdust saturated with 40 parts of trinitroglycerine (Wagner's Jahr. 22, 476).

BRAN. The name given to the coarser fragments, consisting mainly of the outer layers, which are produced in the grinding or milling of cereal or other seeds. When the term is used without any descriptive adjective, the product from wheat is usually understood; but maize, barley, buckwheat, rye, oats, even peas and earth nuts, when milled, yield products which are described as 'bran.'

The following analyses, compiled chiefly from German and American sources, show the general average composition of various 'brans':

—	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
Wheat bran, fine	13·2	15·5	4·8	54·0	8·0	4·5
„ „ coarse	13·2	14·3	4·2	52·2	10·2	5·9
„ „ spring wheat	11·5	16·1	4·5	54·5	8·0	5·4
„ „ winter wheat	12·3	16·0	4·0	53·7	8·1	5·9
Rye bran (German)	12·5	16·7	3·1	58·0	5·2	4·5
„ „ (American)	11·6	14·7	2·8	63·8	3·5	3·6
Barley bran	10·5	14·8	3·6	57·6	8·5	5·0
Oat bran	9·6	7·6	2·7	53·8	21·6	5·7
Maize bran	12·5	9·9	3·6	61·5	9·5	3·0
Rice bran	9·7	12·1	8·8	49·9	9·5	10·0
Buckwheat bran, fine	12·0	15·2	4·5	50·0	11·3	7·0
„ „ coarse	15·6	8·0	1·8	34·2	37·6	2·8
Pea bran	11·7	16·8	1·7	46·2	20·1	3·5
Earth nut bran	10·5	21·8	18·1	24·7	19·5	5·4

The digestion coefficients for the constituents of most varieties of bran are low, so that their food value is in general not so high as the analyses would indicate.

The character and composition of the bran from any particular grain is liable to considerable variation, according to the method of milling adopted. As a rule, the less perfectly the corn is ground, the richer is the bran in meal and therefore in feeding value.

It will be noticed that bran is much richer in protein, fat, ash, and fibre than the fine portions of the meal from the same grain.

In the case of wheat, the finer portions of the bran are known as 'middlings' and 'sharps' or 'shorts.' Usually the last term denotes the portions which most nearly resemble bran, while 'middlings' refers to an intermediate product more approximating to flour in composition, though much richer in protein, ash, and fibre.

The processes employed in the milling of wheat, however, are so complex that about 80 or 100 products are separated. For a study of the composition of the various products of a modern roller mill, *see* Clifford Richardson (Bull. No. 4, U.S. Dept. of Agric. Div. of Chemistry, reproduced in part 9, Bull. 13, [1898]). Usually, about 70 to 75 p.c. of the wheat is obtained as flour of various grades, about 20 p.c. as bran, 3 or 4 p.c. as 'shorts,' and the remainder as screenings and loss.

Weinwurm (Oesterr-Ungar. Zeits. Zuckerind. u. Landw. 1890) found that from Hungarian wheat, 20 p.c. of bran of three degrees of fineness were obtained, possessing the following composition:—

—	Yield p.c.	Water	Composition of dry matter				
			Protein Insol.	Protein Sol. in dil. acetic acid	Fat	Sol. carbohydrates	Fibre	Ash
Fine bran	16	11·35	13·50	3·06	4·54	63·64	8·71	6·55
Medium bran	2	11·55	13·38	2·72	3·96	63·97	9·08	6·89
Coarse bran	2	12·37	13·44	3·17	3·46	62·13	9·79	7·01

Snyder (Studies on Bread and Bread-making at the University of Minnesota, 1901) examined the products from the milling of wheat by the American methods, using a hard Scotch Fife wheat.

The shorts and bran obtained had the following composition:—

	Water	Protein (N×5·7)	Fat	Total carbohydrates	Ash	Acidity
Shorts	8·73	14·87	6·37	65·47	4·56	0·14
Bran	9·99	14·02	4·39	65·54	6·06	0·23

The acidity is expressed in terms of lactic acid.

The carbohydrates of bran have been investigated by Sherman (J. Amer. Chem. Soc,

1897, 19, 291). He found the following average percentages in wheat bran:—

Total soluble carbohydrates calculated as dextrin	7·2 p.c.
Starch	17·7
True pentosans	17·5
Lignin and allied substances	11·6
Cellulose	8·5
Total carbohydrates	62·5

Other investigators — Tollens, Chalmot, Günther and Stone—have found from 22 to 25 p.c. of pentosans in wheat bran, while maize bran contains about 40 p.c.

Girard (Compt. rend. 1897, 124, 926) gives the results of the examination of by-products from wheat—presumably shorts and bran—by a method different from the conventional one.

In estimating the amount of water-soluble matter in products from seeds, he points out the necessity of using ice-cold water, otherwise the enzymes present may act upon the constituents of the seed, and greatly increase the amount of matter soluble in water.

The following are the mean figures calculated from analyses of the by-products from four French wheats:—

Water	Soluble in water	Insoluble in water
14·72	10·63	74·65

The matter soluble in water consisted of—proteids 2·70, carbohydrates 6·16, inorganic matter 1·77. The matter insoluble in water consisted of—gluten 4·55, starch 28·08, nitrogenous woody matter 5·70, fats 3·17, cellulose 30·22, inorganic matter 1·94, loss and undetermined 0·99.

The mineral matter in bran is very high as compared with that in the rest of the seed, being usually between 5 and 6 p.c., whilst that in flour is usually less than 0·5 p.c.

The ash of bran is particularly rich in phosphoric acid, but poor in lime. The following analysis by Wolff gives its usual composition:—

K_2O	Na_2O	MgO	CaO	P_2O_5	SiO_2
24·0	0·6	16·8	4·7	51·8	1·1

There is a widespread belief that bran is particularly well fitted, because of its richness in mineral matter, to supply the needs of animals with reference to the development and nutrition of bone. But from a study of a bone disease among horses and mules in South Africa, it has been deduced that for normal bone nutrition it is necessary that animals be supplied, in their rations, with phosphoric oxide and lime in approximately equal proportions by weight (Ingle, Jour. Comp. Path. and Therapeutics, 1907, March, also Jour. Agric. Science, 1908, 3, 22). From this point of view, bran is particularly ill suited to aid bone development, since it contains an overwhelming preponderance of phosphoric acid over lime, being in the ratio of 100 to 9 in the above analysis, while in some samples it is as high as 100 : 5·5. That bran has an injurious action upon bone nutrition when used in large quantities, is shown by the occurrence of a peculiar bone disease in horses known as 'bran rachitis' or 'millers' horse rickets,' observed in animals fed largely on bran.

The phosphoric acid in bran, however, does not exist entirely as metallic phosphates. According to Patten and Hart (Bull. 250, New York Agric. Expt. Station, 1904) about 68 p.c. of the total phosphorus is extracted by 0·2 p.c. hydrochloric acid solution, and of this, nearly the whole exists as anhydro-oxymethylene diphosphoric acid $C_2H_8P_2O_9$

$$=(OH)_2OPO-CH_2-O-CH_2-OPO(OH)_2$$

a substance first isolated by Posternak (Revue General de Botanique, 1900, 12, 5 and 65; Compt. rend. 1903, 137, 439). In bran, this acid exists in combination with magnesium, calcium, and potassium.

The free acid, when heated with strong mineral acids, is hydrolysed, yielding inositol and phosphoric acid

$$3C_2H_8P_2O_9+3H_2O=C_6H_{12}O_6+6H_3PO_4.$$

Bran is largely used as a food for farm animals, but has a weakening effect upon digestion if used in large quantities. It is more suitable as a food for fattening than for working animals. Owing probably to its mechanical action on the bowels, it has a purgative effect. If used largely for milch cows, it tends to make the butter soft. Similarly, large quantities of bran given to fattening animals tend to lower the melting-point of the body-fat. This is an advantage in the production of mutton or beef, but a disadvantage with bacon.

Bran is also largely used in tanning leather. (For a description of the process and of the changes occurring in the fermentation of bran so employed, *see* Wood and Wilcox, J. Soc. Chem. Ind. 1893, 422, and 1897, 510.) H. I.

BRANDY. (*Eau-de-vie*, Fr.; *Branntwein*, Ger.) The term 'brandy' is an abbreviation of 'brandy-wine' the original English form of the word, which occurs also in all the Teutonic languages of Northern Europe, and signifies burnt or distilled wine. The latter term (wine) in its widest sense includes the product obtained by fermentation of all natural fruit juices or extracts from grain, and not fermented grape juice only. Old English Acts of Parliament refer to 'brandy' and 'aqua vitæ' made from malted corn, whilst the German word *branntwein* is applied to strong potable spirits generally without implying that such spirit is necessarily derived from wine. At the present time, however, the 'brandy' of commerce is almost universally understood to be a spirit derived exclusively from the grape.

Besides alcohol and water, the principal constituents of brandy are acetic, butyric, œnanthic, and valerianic esters, acetic acid, a small quantity of a volatile oil, and a little fixed acid, tannin, and colouring matter. When new, brandy is colourless, but gradually acquires a yellowish-brown colour by storage in oak casks. The required colour for particular brands is, however, usually obtained by the addition of a solution of caramel or burnt sugar. Genuine brandy of good quality has a sweet mellow ethereal flavour, without any suspicion of the 'fiery' or 'earthy' taste common to inferior or fictitious brandies.

The *bouquet* of brandy depends upon (*a*) the nature and quality of the wine from which it has been produced; (*b*) the conditions under which the wine has been fermented; (*c*) the method of distillation employed; and (*d*) the age of the brandy. The characteristic flavour of brandy is said to be due chiefly to œnanthic

ester (ethyl pelargonate), but it varies with the total amount and relative proportions of other volatile constituents present. According to Ordonneau, the peculiar fragrant odour of brandy is due to a very small quantity of a terpene which boils at 178°, and which, on oxidation, gives the characteristic flavour to old brandy.

Over 90 p.c. of the brandy imported into the United Kingdom comes from France, the finest grades being *Cognac* and *Armagnac*, so named from the French towns in which they were originally distilled. But little brandy is now distilled in Cognac itself, the greater part being produced on the brandy farms of the surrounding districts. Other brandies of less value commercially are those of the Midi and the districts of Aude, Gard, Hérault, and Pyrenées Occidentales, commonly known as the 'Trois-six de Montpellier.' Marc brandies are distilled from the fermented 'marc' or refuse of the wine-press as well as from the lees of the wine-casks.

Whilst the term 'Cognac' has by custom come to be used almost as a generic term for 'brandy,' it is, strictly speaking, applicable only to spirits made from wine grown in the Cognac region, which comprises a certain part of the two departments of Charente and Charente Inférieure, also Dordogne and Les Deux-Sévres. A strict delimitation of the Cognac area has been made by the French Government by decree dated 1st May, 1909, and the region is locally subdivided into the Grande or Fine Champagne, the Petite Champagne, the Borderies and the Bois, according to the quality of the wine produced.

The soil of the district is mainly calcareous, and the grape is a small white berry with very acid juice, producing a wine of inferior quality for drinking purposes. (For the extraction and fermentation of the grape juice, *see* WINE.)

As the reputation of the brandies of the Cognac and Armagnac districts depends so much upon their bouquet, they are submitted to slight rectification only, and distillation is therefore usually conducted in a simple 'pot' still by the professional distiller as well as by the farmer. The still, which varies in content from about 150 to 200 gallons, is usually enclosed in brickwork, with only a small bulbous head exposed, and is generally heated by means of a furnace, wood being considered the best fuel. In a few distilleries the stills are heated by steam. Occasionally, a subsidiary vessel, filled with wine and called a 'chauffe-vin,' is attached to the still, and through it the pipe conveying the spirit vapour to the refrigerator passes, heating the wine so that the latter is quickly raised to boiling-point when subsequently passed into the still, thereby effecting a saving of fuel. Two distillations are made, termed 'brouillis' and 'bonne-chauffe,' corresponding respectively with the 'low wines' and 'spirits' of the whiskey distiller.

In some distilleries the finished spirit is produced at one continuous distillation by means of a still described as 'à premier jet.' In this form of still, a vessel is attached to and above the head of the still, and through it the spirit of the first distillation is conveyed. This spirit is again vapourised by the heat of the spirit vapour rising from the still itself on its way to the refrigerator. The spirit produced in this way is not considered so fine as that obtained by the pot still, but it is of higher strength and more suitable for the manufacture of liqueurs.

The quality of the spirit depends greatly on the care with which the distillation process is carried out. The stills should be worked slowly and regularly, the normal time for the complete distillation of a charge being about ten hours.

The quantity of wine used in the process of manufacture is relatively very great, the amount of brandy produced from a given measure being only from 10 to 15 p.c. The strength of the wine varies from 4·5 to 9 p.c. by weight of pure alcohol, or approximately from 10 to 20 p.c. of proof spirit, the average being 6·5 p.c. of alcohol, or 14 p.c. of proof spirit. The finished spirit as run from the still contains about 64 p.c by weight of alcohol, equivalent to a strength of about 25 over-proof. The brandy, as received from the farmers, is blended and diluted in vats, sweetened with cane sugar, slightly coloured with caramel, and filtered (if necessary) into storage vats in which it is matured.

The French Government has by various laws and decrees of the years 1905 to 1909 prohibited the description 'Cognac' to be applied to any mixture of Cognac or other wine spirit, with grain or beet spirit, and has further provided that labels, marks, &c., bearing the word 'Cognac' should signify that the spirit in question is solely the product of the Cognac region (*vide supra*).

The simple pot stills and the modified stills known as 'à premier jet,' above referred to, as being used in the Charente districts, are not suitable for wines having a strong earthy flavour ('terroir') or other undesirable qualities. In such cases, as in the brandies of the Midi, the Rochelle district, and the marc brandies of Burgundy, stills of a more complicated nature are employed, owing to the necessity for a greater degree of rectification. In these the distillation is continuous, and in the Rochelle district and the islands of the N.W. coast, a pot still with a rectifying head, known as the 'Alembic des Iles,' is employed, whilst in the south the distilling column consists of a series of compartments separated by plates or 'plateaux,' connected with taps by means of which it is possible to take off the spirit at a higher or lower strength as desired. These stills are generally heated by direct fire.

Immense quantities of wine are produced in the Midi for conversion into brandy, the grapes of this region being unsuitable for making good wine. This is attributed to the effects of the *Phylloxera*, which devastated the whole of the Charente district in the years 1875–1878. Before this time, most of the brandy exported to the United Kingdom was genuine Cognac, but the destruction of the Charente vineyards stimulated the production of brandy in other parts of France as well as in other countries. The vineyards of the Cognac district were replanted with American stocks, on which Charente vines were grafted, and the result has been highly successful; but in the south of France the vineyards ravaged by the phylloxera were replanted with vines which were not appropriate to the soil, and which yielded wine in great quantity but at the sacrifice of good quality. Hence the use of the rectifying

stills in the Midi and the large quantity of brandy produced. Most of this is consumed in France. The spirit derived from diseased or unsound wines is highly rectified and used for industrial purposes. The cheapness of wine, therefore, affords little or no inducement to the distillers of the Midi to use beet or grain as the raw material for the production of their brandies.

The relative values of the spirits above mentioned may be gathered from the average prices per proof gallon in 1909, which were from 6*s.* for brandy of the best Cognac district (Champagne) to 2*s.* 6*d.* for Bois brandy, the cheapest in the Cognac district, whilst Midi brandy was 1*s.* 9*d.*, and grain and beet spirit 1*s.* 2*d.* and 1*s.* 1*d.* per proof gallon respectively.

Marc brandies or *eaux-de-vie de marc* are, as the name implies, derived from the marc or refuse of the grapes after the juice has been extracted. They have a strong earthy flavour, and usually are very rich in secondary products. They are therefore often added to other wine spirits to impart the brandy character, or admixed with neutral spirit from grain, beet, &c., in the preparation of fictitious brandies.

Algerian brandy is of high quality, resembling Cognac, and is generally sent to France, whence considerable quantities are reshipped from the Charente district to the United Kingdom.

Brandies are produced in most other wine-growing countries, especially when, owing to over-production of wine, or some defect in its quality, it becomes more profitable to convert it into spirit than to dispose of it as 'wine.' The most important commercially are from Spain, Egypt, Germany, South Africa, and Australia, but the quantities of these exported to the United Kingdom are small as compared with French brandies.

The Spanish brandies are similar in character to the French, and command a high price. Genuine Egyptian brandy is made from fresh grapes, although the wine grape is not cultivated in Egypt. The grapes are imported into Alexandria from Southern Turkey, Greece, Cyprus, and Asia Minor, and there made into wine from which the brandy is distilled. They have a strong characteristic flavour, much appreciated by consumers of the cheaper brandies. Spurious brandies of doubtful origin, but described as 'Egyptian,' are also on the market. They are probably made from the currant grape grown in Greece and Asia Minor, and have no right to the title of 'Egyptian,' beyond the fact that they are exported *viâ* Alexandria. Increasing quantities of brandy of fair quality are being produced in South Africa and Australia. The so-called 'dop' brandy of South Africa is produced in the same way as the French 'marc' brandies, and has similar characteristics.

The natural improvement observed in genuine brandies by 'ageing' is always accompanied by a rise in the quantity of the secondary constituents due to the formation of oxidation products (aldehydes and acids) and esters, as well as to concentration due to loss of alcohol and water. The higher alcohols also tend to increase, and furfural to diminish, with age. According to Duplais, the mellowness due to age may be imparted to new brandy, making it fit for immediate use, by adding the following to every 100 litres: old rum, 2·0 litres; old kirsch, 1·75 litres; syrup of raisins, 2·0 litres; and infusion of walnut hulls, 0·75 litre. Low wines which have been kept for some months in casks containing clear rain water preserved by the addition of 10 or 12 p.c. of strong brandy (85°) are also used for a similar purpose.

Whilst there is a legitimate use of colouring which has become practically an essential character of the brandy of commerce, the colour acquired by old brandies owing to long storage in casks is often simulated in order to give to new brandies a fictitious appearance of age by means of a tincture of oak extract obtained from chips, shavings, or sawdust of the white oak used at Cognac for making brandy casks.

Brandy is described in the British Pharmacopœia, as 'Spiritus Vini Gallici,' thus implying the French origin of the spirit, and is defined as 'a spirituous liquid distilled from wine and matured by age, and containing not less than 36½ p.c. by weight, or 43½ p.c. by volume of ethyl hydroxide' (approximately 76 p.c. of proof spirit).

This definition, however, takes no cognisance of the nature, quantity, or relative proportions of the secondary products to which the peculiar medicinal properties of brandy are attributed, and in view of the variations in these constituents even in the brandies of commerce known to be genuine, and the difficulty of arriving at any satisfactory standard, it has been proposed by the British Medical Association to eliminate 'brandy' at the next revision of the Pharmacopœia.

The following standards of purity are prescribed by the United States Pharmacopœia. Brandy should be at least 4 years old; its alcoholic content from 39 to 47 p.c. by weight (81–96 p.c. British proof spirit); specific gravity not exceeding 0·941 nor less than 0·925; the residue should not, on the volatilisation of the last traces of alcohol, evolve a marked disagreeable odour of fusel oil, and should not exceed 1·5 p.c.; also the residue from 100 c.c. should dissolve readily in 10 c.c. of cold water, and should be free from more than traces of tannin (*i.e.* should not give more than a pale-green colouration on the addition of a dilute solution of ferric chloride); and the acidity should require not more than 1 c.c. of decinormal alkali for neutralisation using phenolphthaleïn as an indicator.

Under the Sale of Food and Drugs Act, no standard for brandy is fixed beyond the limitation of strength (in common with whiskey and rum) to a minimum of 25 p.c. under proof, below which it may not legally be sold without the fact of dilution being declared. The strength of brandy as imported into the United Kingdom varies considerably, but the average is about 5° below proof, or 46·5 p.c. of alcohol by weight.

Ordonneau (Compt. rend. 102, 217) subjected 100 litres of 25-year-old brandy to fractional distillation, and obtained the following substances estimated in grams per hectolitre:—

Aldehyde	3·0
Normal propyl alcohol	40·0
Normal butyl alcohol	218·6
Amyl alcohol	83·8
Hexyl alcohol	0·6
Heptyl alcohol	1·5
Acetic ester	35·0

Propionic, butyric, and caproic esters	3·0
Œnanthic ester (about)	4·0
Acetal and amines	traces

Morin (Compt. rend. 105, 1019) distilled 92 litres of pure cognac in Claudin and Morin's apparatus. The first portion of the distillate contained the more volatile bodies; the second consisted of tolerably pure ethyl alcohol; the third, the higher-boiling alcohols, &c. The residue, chiefly water, was tested for free acids, *iso*butylglycol and glycerol.

The first three portions were then fractionated, 5 litres of light alcohol, 55 litres of pure ethyl alcohol, and 3·5 litres of higher-boiling compounds being obtained. The latter fraction smelt strongly of fusel oil, and possessed a burning taste. The water remaining behind was added to that already obtained. The fractions were then redistilled in Le Bel and Henninger's apparatus. The fusel oil portion, which after dehydration by potassium carbonate weighed 352 grams, gave:

	grams
Water	7
Ethyl alcohol	130
Normal propyl alcohol	25
*Iso*butyl alcohol	6
Amyl alcohol	175
Furfural	2
Wine oils	7

The water contained a little acetic and butyric acids, and a small quantity of a viscous liquid which distilled undecomposed under diminished pressure, and appeared to consist of *iso*butyl alcohol and glycerol. The residue contained tannin, together with substances extracted from the wood.

In the following table: 1 shows the compounds contained in 100 litres of the cognac; 2 shows the same obtained by the fermentation of 100 kilos. of sugar:—

	1 grams	2 grams
Aldehyde	trace	trace
Ethyl alcohol	50,837·00	50,615·0
Norm. propyl alcohol	27·17	2·0
*Iso*butyl alcohol	6·52	1·5
Amyl alcohol	190·21	51·0
Furfural bases	2·19	—
Wine oil	7·61	2·0
Acetic acid	trace	—
Butyric acid	trace	—
*Iso*butyl glycol	2·19	—
Glycerol	4·38	—

Butyl alcohol was absent; furfural was detected directly by the addition of aniline to the cognac, a red colouration being produced in the presence of acetic acid. It will be observed that *iso*butyl alcohol is present only in small quantity, whilst in Ordonneau's results it is absent altogether.

The analytical data usually relied upon for discriminating between genuine brandies and those blended with neutral spirit are (*a*) volatile acids; (*b*) aldehydes; (*c*) esters; (*d*) higher alcohols; and (*e*) furfural. The results are calculated in parts per 100,000 of absolute alcohol, *e.g.* in milligrams per 100 c.c., or grams per hectolitre. The total amount of the secondary products expressed in this manner is termed the 'coefficient of impurities,' or preferably the 'coefficient non-alcohol.' The standard coefficient suggested by Girard and Cuniasse for genuine brandy is 300, of which not less than 80 should be esters. In calculating the proportion of neutral spirit in a mixture, allowance should be made for the small amount of secondary products present in neutral spirit. The average coefficient for industrial alcohol, as shown by the analyses of Girard and Cuniasse, is 17 and the esters 8.

(For a detailed description of the methods of analysis employed, *see* Thorpe, Minutes of Evidence taken by the Royal Commission on Whiskey and other Potable Spirits, ii. Appendix Q, xii. 1909.)

The causes which affect the characteristic bouquet of the wine naturally influence the proportion as well as the character of the volatile matters included in the 'coefficient' of the brandy. Thus the proportion of acids and esters is considerably augmented if the wine becomes sour, and, speaking generally, the aldehydes are higher in white than in red wines. Also in regard to distillation, the aldehyde and more volatile esters are found mainly in the first runnings ('produits de tête'), whilst the higher alcohols and furfural occur in largest quantity in the tailings ('produits de queue').

In the brandies of Charente and Armagnac the coefficient is usually rather high, but ordinarily, in cognacs and *fine champagne*, it ranges between 275 and 450, although occasionally it falls considerably beyond these limits. Brandies obtained from wines of the Midi and from Algeria show much wider variations, ranging from 25 (indicating strong rectification) to 500. Marc brandies have almost invariably a very high coefficient, ranging from 500 to nearly 1500, and in these, aldehydes often form a large proportion.

Attempts have been made to fix minimum and maximum values for the coefficient, but without much success, the former with a view to the detection of the admixture of neutral spirit, and the latter to restrict the amount of secondary products for hygienic reasons. The effect of such limits would be to condemn many brandies that are undoubtedly genuine and even of high commercial value.

From the hygienic point of view, the esters, furfural, and especially the aldehydes, have a much more deleterious action on the human system than the higher alcohols, whilst the acids, particularly acetic, which frequently forms a large proportion of the coefficient, cannot be said to have any detrimental influence.

The French Government, in 1904, instituted an inquiry by the Technical Committee of Œnology into the possibility of fixing standards for the total amount of secondary products ('coefficient non-alcohol') of genuine brandy, but the conclusion arrived at was that neither a minimum nor a maximum limit could be recommended owing to the extremely variable character of brandy, not only with respect to the coefficient as a whole, but also in regard to the proportions of the volatile constituents relatively to each other. Chemical analysis should not be relied upon alone, but should be supplemented and its results confirmed by expert tasting ('degustation').

British brandy is usually made from grain spirit distilled with certain flavouring materials,

or by adding flavouring ingredients to the spirits. It is frequently mixed with foreign brandy, and is largely used for cooking purposes.

The following is Ure's recipe for British brandy: 'Dilute the pure alcohol to proof pitch and add to every 100 pounds weight of it from half a pound to a pound of argol—crude tartar—dissolved in water, some bruised French plums, and a quart of good cognac. Distil this mixture over a gentle fire in an alembic provided with an agitator. The addition of brandy and argol introduces œnanthic ether, and if a little acetic ether be added to the distillate, the whole imparts the peculiar taste of genuine Cognac brandy. Colour with burnt sugar, if necessary, and add a little tannic acid to impart astringency.'

Amongst the flavouring ingredients used in the manufacture of artificial brandies (including British brandy) may be mentioned the following: œnanthic ester, tincture of catechu, balsam of tolu, acetic ester, argol, cognac oil, essence of cognac, infusions of bitter almond shells, tea, and walnut hulls, liquorice root, prune juice, rum, syrup of raisins, vanilla, &c. So-called 'cognac essences' contain mixtures of the aromatic compounds just mentioned, whilst 'cognac oil' is made by the distillation of a mixture of alcohol, coco-nut oil, and sulphuric acid, œnanthic ester being one of the products.

As a simple formula for artificial brandy of the cheapest grade, Fleischmann gives the following: spirits, 45 gallons; caramel, 6 ozs.; cognac oil, ⅛ oz.

Cider brandy is manufactured in the United States and Canada from cider and perry.

Danzig brandy is made from rye ground with the root of *Calamus aromaticus*.

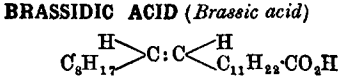
Guernsey brandy is the spirit of beet root flavoured to imitate true brandy.

Hamburg brandy is said to consist of potato or beet-root spirit as a basis, flavoured with essences or by the addition of inferior brandy, and coloured to represent genuine brandy. Similar imitation brandies appear to be made in the north of France, in Belgium, and in other foreign countries. (Girard and Cuniasse, Man. pratique de l'Analyse des Alcools et des Spiritueux; Schidrowitz: Analyst, June, 1905, and June, 1906; Thorpe, Nature, 3 Nov. 1904; and Report of Royal Commission on Whiskey and other Potable Spirits, 1908–9.) J. C.

BRASS *v.* ZINC.

BRASSIC ACID *v.* BRASSIDIC ACID.

BRASSIDIC ACID (*Brassic acid*)



is isomeric with erucic acid (*q.v.*), from which it may be obtained by the action of nitrous acid (Haussknecht, Annalen, 143, 54; Reimer and Will, Ber. 1886, 3321; Websky, Jahrb. Chem. 1853, 444; Fitz, Ber. 1871, 444); by treatment with hydrogen bromide in acetic acid solution, monobrombehenic acid $C_{22}H_{43}O_2Br$, being also formed (Ponzio, Gazz. chim. ital. 35, ii. 394); and by heating with concentrated sulphurous acid at 200° (M. K. and A. Saytzew, J. Russ. Phys. Chem. Soc. 24, 482; J. pr. Chem. 50, [2] 78). It may also be obtained by heating behenolic acid with zinc and acetic acid, and a few drops of hydrochloric acid (Holt. Ber. 1982, 962), and by the reduction of monobrombrassidic acid, which is obtained by treating behenolic acid with hydrogen bromide (Hasse and Stutzer, Ber. 1903, 3601). Brassidic acid crystallises from alcohol in plates, m.p. 65°–66° (Saytzew, *l.c.*), b.p. 282°(30 mm.), 265° (15 mm.), 256° (10 mm.), 180° (0 mm.), (Krafft and Weilandt, Ber. 1896, 1325); sp.gr. 0·8585 at 57·1°/4°; is less soluble than erucic acid in alcohol and ether. (For relationship to erucic acid and comparison of their behaviour towards various reagents, *v.* Albitzky, J. Russ. Phys. Chem. Soc. 31, 76; 34, 788; J. pr. Chem. 61, [2–3] 65.) By fusing brassic acid with potash, arachidic acid $C_{20}H_{40}O_2$ is obtained (Goldschmidt, Jahrb. Chem. 1877, 728); oxidation with potassium permanganate yields a dihydroxybehenic acid (Jukovsky, J. Russ. Phys. Chem. Soc. 24, 499; Albitzky, *l.c.*). Treatment with hydriodic acid in glacial acetic acid yields iodobehenic acid (Bayer and Co., D. R. P. 180087; Chem. Soc. Abst. 1907, i. 380).

BRASSIL. A local name for iron pyrites.

BRASSYLIC ACID $C_{13}H_{24}O_4$. Obtained, together with other products, by acting on behenolic acid $C_{22}H_{40}O_2$, with fuming nitric acid (Haussknecht, Annalen, 143, 45; Grossmann, Ber. 1893, 644). May be prepared by the action of nitric acid on erucic acid (Fileti and Ponzio, Gazz. chim. ital. 23, ii. 393), and from ικ-undecenoic acid (Krafft and Seldis, Ber. 1900, 3571). Flat needles; m.p. 113°–114°; readily soluble in alcohol and ether, sparingly soluble in water.

BRAUNITE. A manganese mineral classed with the oxides, but containing an appreciable amount of silica (8–10 p.c.), the formula being $3Mn_2O_3{\cdot}MnSiO_3$ or $4Mn_2O_3{\cdot}MnSiO_3$. The manganese is usually isomorphously replaced by small amounts of iron, calcium, barium, &c. It is generally found in compact masses, but sometimes as tetragonal pyramids, the angles of which are very near to those of the regular octahedron. The crystals possess a perfect pyramidal cleavage. The colour is black with a sub-metallic to metallic lustre. Sp.gr. 4·8; H. 6–6½. The mineral is found in the manganese-mines in Sweden; and, with the exception of psilomelane, it is the most abundant of the manganese ores in India (*v.* L. L. Fermor, Mem. Geol. Survey, India, 1909, XXVII). L. J. S.

BRAZIL NUTS are the fruits of *Bertholletia excelsa* (Humb. and Bonp.). They yield 73 p.c. of a fatty oil of pale yellow colour, of a taste similar to that of the nuts themselves. The oil is expressed from mouldy nuts only, as the sound nuts have too high a value for edible purposes to be used for the manufacture of a fatty oil. J. L.

BRAZILETTO. An inferior kind of Brazilwood obtained from *Cæsalpinia braziliensis* (Linn.), growing in the West Indies.

BRAZILWOOD. Under the name of Brazilwood certain varieties of the so-called 'soluble' red woods are known, the term 'soluble' being employed to distinguish them from the dyestuffs of the barwood class, which only with difficulty yield their colouring matters to boiling water. These soluble red woods give with aluminium mordanted fabrics, a bright-red shade, which in each case is derived from one and the same colouring matter, and all are botanically allied, in that they consist of the wood of various species of *Cæsalpinia*. About nine varieties

have been employed as dyestuffs, of which the following are the best known :—

Fernambuco or *Pernambuco wood* is considered to be the richest in colouring matter, and is the product of the *Cæsalpinia crista*, a tree which is abundant in Jamaica and Brazil.

The true *Brazilwood* is derived from the *Cæsalpinia braziliensis*, and is said to contain only one-half the colouring matter which is present in the Fernambuco variety. It is obtained exclusively from Brazil.

Sappanwood is obtained from the *Cæsalpinia sappan*, a tree which is common to the warmer regions of Asia. The so-called *Limawood* is a variety of sappan, and the dyewood imported from the Philippine Islands is an inferior quality of this product.

Peachwood is the product of the *Cæsalpinia echinata*, which occurs in Central America and the northern parts of South America.

These woods, which are very hard, and of a deep-red colour, come into the market in the form of billets varying in weight from a few pounds up to a hundredweight. If freshly cut, the internal colour of the wood is seen to be light-yellow, but this soon changes to deep-red in contact with air.

Some varieties of these woods were employed for dyeing purposes in India long before the discovery of America, and it is stated that when South America was discovered by the Spaniards, in 1500, the northerly portion of the country was named Brazil (from *braza*, fiery red), because this red dyewood was found there in such immense quantities.

Owing to the fugitive character of the colours yielded by Brazilwood, it is now only employed to a somewhat limited extent.

Brazilin $C_{16}H_{14}O_5$, the colouring principle of Brazilwood, was first isolated in a crystalline condition by Chevreul (Ann. Chim. Phys. [1] 66, 225); but was not further examined until 1864, when Bolley (Schweiz. poly. Zeitsch. ix. 267) assigned to it the formula $C_{22}H_{20}O_7$. Subsequently Kopp (Ber. 6, 446) proposed the formula $C_{22}H_{18}O_7$, but it was left to Liebermann and Burg (Ber. 9, 1883) to determine the exact composition of this substance, and their formula, $C_{16}H_{14}O_5$, is in use at the present time. To prepare brazilin from the wood itself, it is best to employ the commercial extract. This is stirred up with a considerable quantity of sand, the product extracted with cold ether, the ethereal liquid evaporated to a small bulk, treated with a little water, and allowed to stand for some days. Crystals slowly separate, and these are purified by crystallisation from a little water.

This method is, however, tedious, and the usual source of brazilin consists of the crude crystalline crusts of this substance which are frequently deposited from Brazilwood liquor, an intermediate product in the manufacture of Brazilwood extract. The crude substance is best purified by two or three crystallisations from water, to which a little sulphurous acid has been added (Gilbody and W. H. Perkin, and Yates, Chem. Soc. Trans. 1901, 79, 1396). Brazilin crystallises in two forms, either as colourless needles containing $1\frac{1}{2}H_2O$, or as colourless prisms with $1H_2O$. It is readily soluble in alcohol and water, and dissolves in dilute soda solution with a beautiful carmine-red colour.

Tetraacetylbrazilin $C_{16}H_{10}O_5(C_2H_3O)_4$, colourless needles, m.p. 149°–151° (Liebermann and Burg); *triacetylbrazilin* $C_{16}H_{11}O_5(C_2H_3O)_3$, needles, m.p. 105°–106° (Buchka and Erck, Ber. 18, 1139); *brombrazilin* $C_{16}H_{13}BrO_5$, brown-red leaflets (B. and E.): *dibrombrazilin* $C_{16}H_{12}Br_2O_5$, leaflets (Schall and Dralle, Ber. 23, 1550); *tetraacetylbrombrazilin* $C_{16}H_9BrO_5(C_2H_3O)_4$, needles, m.p. 203°–204° (Buchka, Annalen, 17,685); *tetraacetyldibrombrazilin* $C_{16}H_8Br_2O_5(C_2H_3O)_4$, m.p. 185° (S. and D.); *tribrombrazilin* $C_{16}H_{11}Br_3O_5$ (S. and D.); *dichlorbrazilin* $C_{16}H_{12}Cl_2O_5$ (L. and B.); and *tetrabrombrazilin* $C_{16}H_{10}Br_4O_5$, fine red needles (B. and E.) have been prepared.

When brazilin is methylated with methyl iodide in the usual manner, it gives *brazilin trimethyl ether* (S. and D. Ber. 20, 3365; Herzig, Monatsh. 14, 56: and Schall, Ber. 27, 525) $C_{16}H_{11}O_2(OCH_3)_3$, prisms, m.p. 138°–139°; and on acetylation yields *acetylbrazilin trimethyl ether* $C_{16}H_{10}O_2(OCH_3)_3(C_2H_3O)$, m.p. 171°–173° (Herzig, Monatsh. 15, 140; Schall, Ber. 27, 326).

According to Gilbody, Perkin, and Yates (Chem. Soc. Trans. 79, 1403), large quantities of the trimethyl ether are conveniently prepared as follows: 143 grams of brazilin dissolved in the smallest possible quantity of methyl alcohol, are treated with 35 grams of sodium in methyl-alcohol and methyl iodide (250 grams), and the mixture is heated 50 hours to 60°–55° in absence of air. A second method employed also by Kostanecki and Lampe (Ber. 35, 1669) consists in methylating brazilin with excess of dimethylsulphate and alkali.

The difficulty experienced in fully methylating brazilin is evidence of the presence of an alcoholic group; but the tetramethyl ether $C_{16}H_{10}O(OCH_3)_4$, m.p. 137°–139°, has been prepared by Schall by treating the sodium compound of the trimethyl- derivative suspended in benzene with methyl iodide at 120° (compare also Herzig, *l.c.*). From this substance the following derivatives have been prepared :—

Brombrazilin tetramethyl ether $C_{16}H_9BrO\cdot(OCH_3)_4$, prisms, m.p. 180°–181° (S. and D. Ber. 21, 3014); and *dibrombrazilin tetramethyl ether* $C_{16}H_8Br_2O\cdot(OCH_3)_4$, m.p. 215° (S. and D. Ber. 23, 1432).

When brazilin is submitted to dry distillation, it gives *resorcin* (Kopp, *l.c.*), and by fusing it with potassium hydroxide, Liebermann and Burg obtained resorcin, and Herzig (Monatsh. 27, 739) also *protocatechuic acid*. With nitric acid brazilin yields *trinitroresorcinol* (Reim, Ber. 4, 334).

When brazilin, the colouring principle, is oxidised under suitable conditions, it is converted into *brazilein*, the true colouring matter

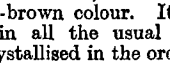
$$C_{16}H_{14}O_5+O=C_{16}H_{12}O_5+H_2O$$

and for this purpose the action of air on an alkaline brazilin solution, alcoholic iodine (Liebermann and Burg), potassium nitrite, and acetic acid (Schall and Dralle), nitric acid in the presence of ether (Buchka and Erck), and sodium iodate (Mayer, Centralb. 1904, i. 228) have been employed. It can, however, be more economically prepared from Brazilwood extract in the following manner (Hummel and Perkin, Chem. Soc. Trans. 1882, 41, 367).

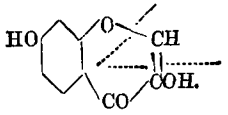
To an aqueous solution of the extract, an excess of ammonia is added, and air is aspirated

through the liquid. A precipitate of the impure ammonium salt of brazilein gradually separates, and this is collected, dissolved in hot water, and treated with dilute acetic acid (sp.gr. 1·04). A brown viscous precipitate of the crude colouring matter is thus obtained, and this is extracted with hot dilute acetic acid, and the extract evaporated on the water-bath. Crystals of brazilein separate, which are collected and washed with acetic acid.

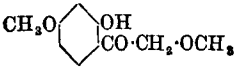
Brazilein consists of minute plates possessing a strong metallic lustre, and by transmitted light a reddish-brown colour. It is very sparingly soluble in all the usual solvents, and cannot be recrystallised in the ordinary manner. It is in reality the colouring matter of Brazilwood, and possesses strong tinctorial property. Alkaline solutions dissolve it with a deep-red colouration, which on standing in air passes gradually to brown. A study of this oxidation was carried out by Schall and Dralle, with interesting results. 2·7 grams of brazilin dissolved in 150 c.c. of water was treated with 10 c.c. of sodium hydroxide solution (sp.gr. 1.37), and air aspirated through the liquid for 36 hours. Ether extracted from the acidified solution *β-resorcylic acid*, and a substance $C_9H_6O_4$, crystallising in brownish-yellow needles, m.p. 271°, which gave a *diacetyl* compound, m.p. 148°–149°, and a *dimethyl* ether, m.p. 169°–170°. When the latter was oxidised in acetic acid solution, with potassium permanganate *β-resorcylic acid monomethyl ether* was produced:



Schall and Dralle considered that this compound was probably a pheno-γ-pyrone derivative, and Feuerstein and Kostanecki (Ber. 32, 1024) proved that this was in reality the case, and assigned to it the following constitution :—



Thus the dimethyl ether, when hydrolysed with alcoholic potash, gave *fisetol dimethyl ether*

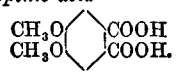


a substance which had already been obtained in a similar manner by Herzig from fisetin tetramethyl ether (*see* Young Fustic).

Our chief knowledge of the constitution of brazilin is due to the elaborate investigations of W. H. Perkin and his pupils, who obtained most important results by the oxidation of brazilin trimethyl ether with potassium permanganate, and also with chromic acid.

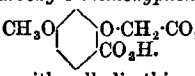
Gilbody, Perkin and Yates (Chem. Soc. Trans. 1901, 79, 1465) found that when brazilin trimethyl ether is oxidised with permanganate, it gives, in addition to oxalic, acetic, and formic acids, the following compounds :—

1. *m-Hemipinic acid*



The isolation of this substance was important, since it showed that brazilin contains a catechol nucleus and two orthohydroxyls, as a result of which no doubt in part its tinctorial properties are due.

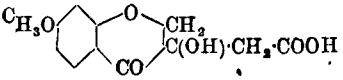
2. *2-Carboxy-5-methoxyphenoxyacetic acid*



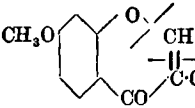
On fusion with alkali, this compound yields resorcinol, and on heating with water to 200° is converted into *methoxyphenoxyacetic acid*

This can be synthesised by the interaction of ethylbromacetate and the sodium compound of resorcinol monomethyl ether and subsequent hydrolysis.

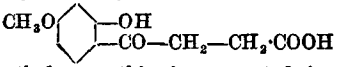
3. *Brazilic acid*



when fused with alkali, gives resorcin, and on warming with sulphuric acid is converted into *anhydrobrazilic acid*

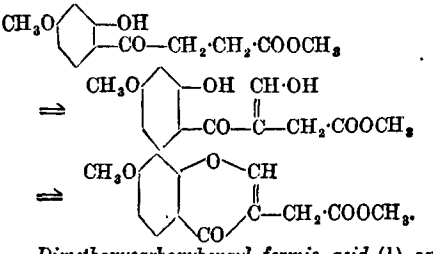


Boiling baryta water hydrolyses anhydrobrazilic acid, with production of *formic acid* and *6-hydroxy-4-methoxybenzoylpropionic acid*

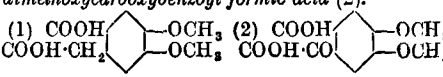


On methylation this is converted into the dimethyl ether, and the latter can be produced by the interaction of dimethyl resorcinol and the half-chloride of succinic acid monoethyl ester, and subsequent hydrolysis. It is also formed when resorcinol dimethyl ether and succinic acid are treated with aluminium chloride without employing a solvent.

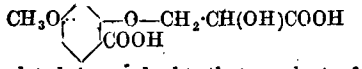
Finally, when the methyl ester of this hydroxymethoxybenzoylpropionic acid is dissolved in ethyl formate and treated with sodium, the *methyl ester* of *anhydrobrazilic acid* is produced. This interesting synthesis may be represented as follows :—



Dimethoxycarboxybenzyl formic acid (1), and *dimethoxycarboxybenzoyl formic acid* (2).

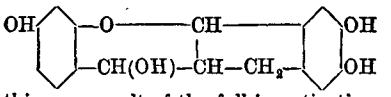


represent intermediate stages in the formation of *m*-hemipinic acid from brazilin trimethyl ether, whereas the acid



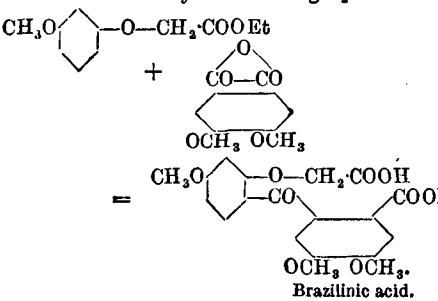
also isolated, is, no doubt, that product of the oxidation which is anterior to the formation of carboxymethoxyphenoxyacetic acid (*see* above).

The earlier work suggested the following probable constitution for brazilin :—



but this, as a result of the full investigation and synthesis of brazilinic acid, a very important substance, also produced by the oxidation of brazilin trimethyl ether, was subsequently discarded.

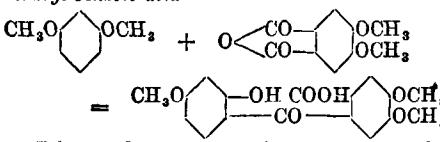
Brazilinic acid. The constitution of this acid has been conclusively demonstrated by its synthesis, which has been effected by the interaction of *m*-hemipinic anhydride with ethyl methoxyphenoxyacetate in the presence of aluminium chloride. This is illustrated by the following equation :—



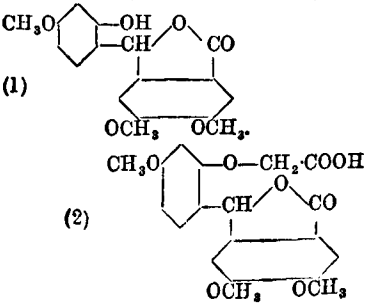
Brazilinic acid.

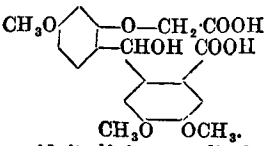
When brazilinic acid is reduced with sodium amalgam, it is quantitatively converted into *dihydrobrazilinic acid* $C_{19}H_{20}O_9$, which at once loses water with the formation of the *lactone* $C_{19}H_{18}O_8$.

To synthesise the latter compound, *m*-hemipinic anhydride is condensed with resorcinol dimethyl ether to form *2'-hydroxy-4.5.4'-trimethoxybenzoyl benzoic acid*



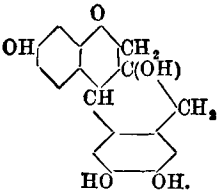
When reduced with sodium amalgam, this acid gives *2-m-meconyl-5-methoxyphenol* (1), and this by the action of chloracetic acid and potassium hydroxide is converted into the lactone of dihydrobrazilinic acid (2)





Dihydrobrazilinic acid itself is accordingly represented by formula (3).

The following constitution :—



has, as a result of this work, been assigned to brazilin by Perkin and Robinson (Chem. Soc. Trans. 1908, 93, 496), and is in complete harmony with the facts above enumerated.

Oxidation of trimethylbrazilin with chromic acid.

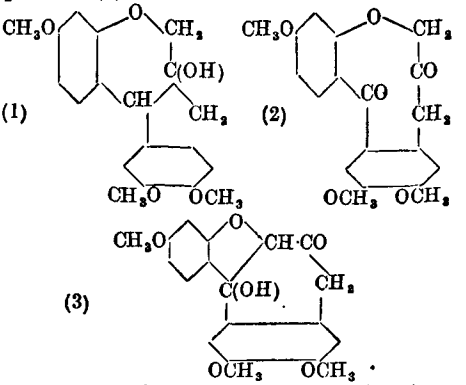
When trimethylbrazilin is oxidised with chromic acid it is converted into *trimethylbrazilone* (Gilbody and Perkin, *v. infra*).

$(CH_3O)_3C_{16}H_{11}O_2+2O=(CH_3O)_3{\cdot}C_{16}H_9O_3+H_2O$

and this apparently simple reaction has proved to be of an extremely puzzling character.

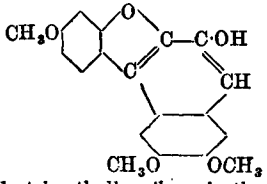
When trimethyl brazilone is oxidised with permanganate, it gives *m-hemipinic acid, 2-carboxy-5-methoxyphenoxyacetic acid, brazilic acid, dimethoxycarboxybenzoylformic acid, dimethoxycarboxybenzylformic acid, methoxycarboxyphenoxylactic acid,* and *brazilinic acid.*

In an earlier paper, Gilbody and Perkin (Chem. Soc. Trans. 1902, 81, 1040) suggested for trimethylbrazilone a constitution based upon their first formula for brazilin (*see* above), but it has now been shown that the reaction proceeds in the following manner (*ibid.* 1908, 93, 498). By the oxidation of trimethylbrazilin (1) with chromic acid a disruption of the central linkage occurs, with the formation of an unstable diketone (2), and this subsequently undergoes aldol condensation, and trimethylbrazilone is produced (3).



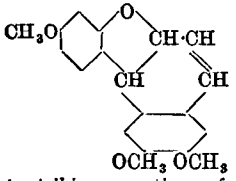
This formula represents trimethylbrazilone as a derivative of *tetrahydronaphthalene,* and affords a ready explanation of the decomposition products of this compound.

An important point in favour of this constitution is afforded by the behaviour of trimethyl brazilone with alkalis or acetic anhydride and other dehydrating agents, for it is thus converted with loss of one molecule of water into *anhydrotrimethylbrazilone* $(CH_3O)_3C_{16}H_7O_2$. There can be little doubt that the formation of this substance is due to the elimination of water from the aldol grouping in trimethylbrazilone, and that it possesses the following formula :—



Anhydrotrimethylbrazilone is thus a derivative of *β-naphthol*, and it possesses many of the properties of this substance. It is soluble in dilute alkali, and this solution gives with diazobenzene chloride a red azo- dyestuff. Diazonaphthalene chloride behaves similarly, and the dye thus produced dissolves in sulphuric acid with a blue colour.

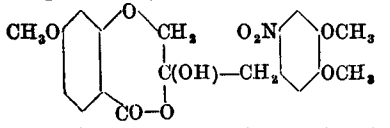
When trimethylbrazilone is boiled in acetic acid solution with phenylhydrazine, *deoxytrimethylbrazilone* $C_{16}H_9O_3(CH_3O)_3$ is obtained, and this is probably a dihydronaphthalene derivative of the formula



The most striking reaction of trimethylbrazilone is its behaviour with nitric acid, when it yields *nitrohydroxydihydrotrimethylbrazilone*

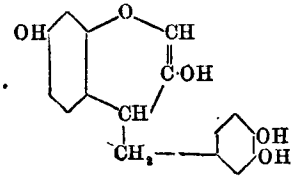
$C_{16}H_9O_3(CH_3O)_3 + HNO_3 = C_{16}H_{10}O_6N(CH_3O)_3$

This substance dissolves in alkali with a purple colour, but on standing the colour rapidly fades, *o-nitrohomoveretrol* separates, and the solution contains *p-methoxysalicylic acid*. Oxidation with permanganate gives *2-carboxy-5-methoxyphenoxyacetic acid*, and these decompositions point clearly to the formula



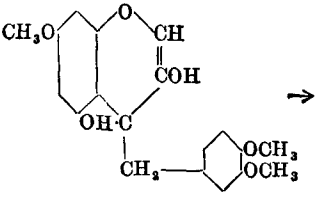
as representing the constitution of the nitrocompound. (*See also* Perkin and Robinson, *ibid.* 1909, 95, 381.)

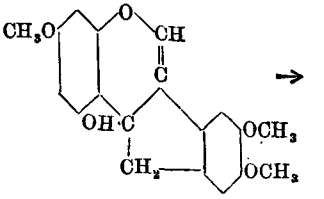
Feuerstein and Kostanecki (Ber. 32, 1024) assigned the following constitution to brazilin:—

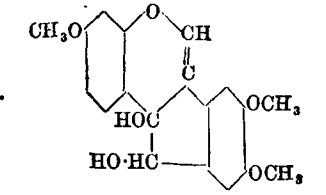


which was based upon the production of dihydroxypheno-γ-pyrone (Schall and Dralle), by its alkaline oxidation and of protocatechuic acid by fusion with alkali (Herzig).

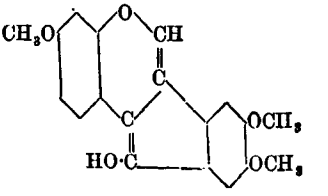
It was, however, pointed out by Perkin that this formula does not account for the presence of *m*-hemipinic acid among the oxidation products of trimethylbrazilin, and Herzig and Pollak (Monatsh. 1901, 22, 207) advanced a similar criticism. On the other hand, it was suggested by Kostanecki and Lampe (Ber. 1902, 35, 1667) that *m*-hemipinic acid was not to be regarded as an oxidation product of trimethylbrazilin itself, but that it arose from the formation during the oxidation of a phenanthrene- or indene- derivative, which by the further action of the permanganate gives this acid. Such an indene- condensation is illustrated by the following scheme, which, according to these authors, probably occurred during the formation of trimethylbrazilone from trimethylbrazilin. The first product of the oxidation with chromic acid will possess the formula I., and this is converted by the following stages into trimethylbrazilone III.

I. 

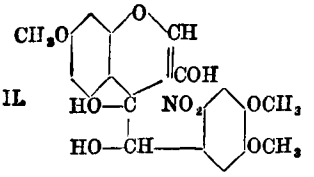
II. 

III. 

This constitution accounts in a simple manner for the formation of the anhydrotrimethylbrazilone I., and the nitrohydroxydihydrotrimethylbrazilone II. of Perkin, which can be represented as follows :—

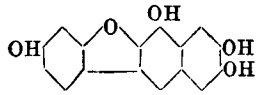
I. 

II.

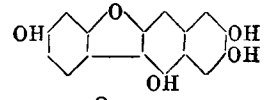


When anhydrotrimethylbrazilone is digested with hydriodic acid, anhydrobrazilone $C_{16}H_{10}O_5$ $+H_2O$ is produced, but when trimethylbrazilone itself is treated in a similar manner, the result is of a peculiar nature. The compound $C_{16}H_8O(OH)_4$ so obtained does not consist of brazilone, but possesses the formula (I.) or (II.), and on distillation with zinc-dust gives *brazan* (III.) (Kostanecki and Lloyd Ber. 1903, 36 2193).

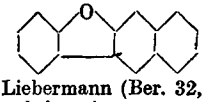
I.



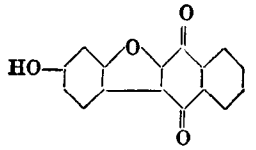
II.



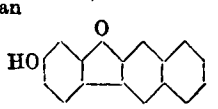
III.



In 1899 Liebermann (Ber. 32, 924) obtained anhydro-*a*-naphthoquinone resorcin by the condensation of 2-3-dichlor-*a*-naphthoquinone with resorcin

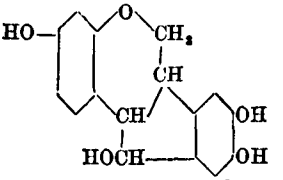


and this, according to Kostanecki and Lampe (Ber. 1908, 41, 2373), is 3-hydroxybrazanquinone. By reduction with hydriodic acid, this gives hydroxybrazan



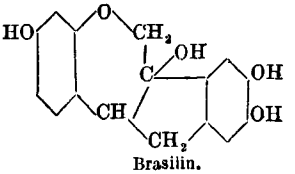
and from this latter or from the quinone itself, brazan, identical with that obtained from trimethylbrazilone, is produced. Brazan crystallises in leaflets, and melts at 202°.

Kostanecki and Lampe (Ber. 1902, 35, 1674) have considered it probable that, after all, trimethyl brazilin does contain, as found by Perkin, a nucleus which on oxidation yields hemipinic acid, and appear to have adopted the following as their final formula for brazilin :—

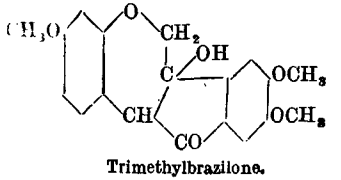


This constitution, it is evident, will still harmonise with the formulæ of trimethylbrazilone and anhydrotrimethylbrazilone given above by these authors.

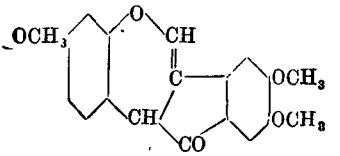
Herzig and Pollak (Ber. 1903, 36, 398) suggested the following constitution for brazilin, trimethylbrazilone, and anhydrotrimethylbrazilone :—



Brasilin.

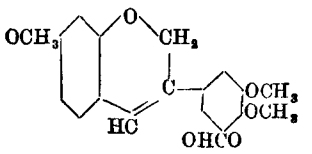


Trimethylbrazilone.

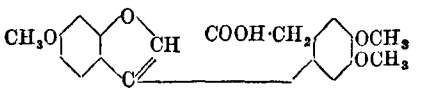


Anhydrotrimethylbrazilone.

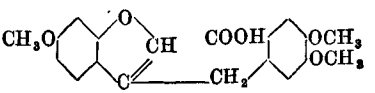
Somewhat later Herzig observed that (Ber. 1904, 37, 631) that trimethylbrazilone undergoes isomeric change when it is dissolved in sulphuric acid, and yield-*γ-trimethylbrazilone* $C_{16}H_9O_3(OCH_3)_3$, m.p. 170°–173°, to which the formula



was assigned (Herzig and Pollak, Monatsh. 1906, 27, 743). Perkin and Robinson (*l.c.*) find that on oxidation with permanganate this compound gives large quantities of *2-carboxy-4-5-dimethoxyphenylacetic acid* $(CH_3O)_2{\cdot}C_6H_2{\cdot}(COOH){\cdot}CH_2{\cdot}COOH$, and that there can be little doubt that its true constitution is represented by one of the formulæ

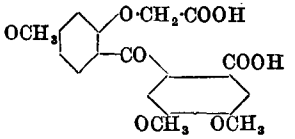


or



Finally, Herzig and Pollak (Monatsh. 1906, 27, 743) have considered it necessary to modify their first formula for brazilin, and have arrived at the conclusion that that latterly proposed by Kostanecki and Lampe correctly represents this colouring principle. The more recent work of Perkin and Robinson detailed above shows, however, that this constitution cannot be correct,

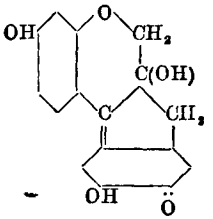
because it does not account for the production of brazilinic acid by the oxidation of trimethylbrazilin



and there is every reason to consider that the formula suggested by the latter authors is the correct representation of the constitution (*cf.* also Perkin and Robinson, Chem. Soc. Trans. 1909, 95, 381) of brazilin.

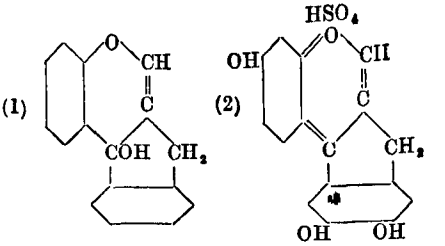
Brazilein yields a triacetyl derivative $C_{16}H_9O_5(C_2H_3O)_3$, yellow leaflets, m.p. 203°–207° (Schall and Dralle, Ber. 23, 1434), and a trimethyl ether $C_{16}H_9(OCH_3)_3O_2$, which crystallises in two modifications, melting at 160° and 178° respectively (Engels and Perkin, Chem. Soc. Proc. 1906, 22, 132). Brazilein trimethyl ether combines with formic acid, yielding a formic acid derivative which crystallises in garnet-coloured prisms, and is decomposed into its components by treatment with alcohol.

The constitution assigned to brazilein by Perkin is as follows :—

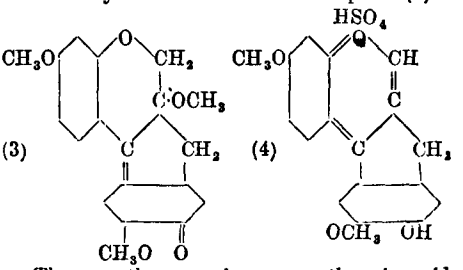


When brazilein is dissolved in sulphuric acid, and the solution is diluted with acetic acid, minute orange-red prisms of *isobrazilein sulphate* $C_{16}H_{11}O_4{\cdot}SO_4H$ separate (Hummel and A. G. Perkin, Chem. Soc. Trans. 1882, 41, 367), and this, on treatment with alcohol, gives the basic sulphate $C_{16}H_{12}O_5(C_{16}H_{11}O_5{\cdot}SO_4H)_2$, which crystallises in red needles. Hydrochloric and hydrobromic acids at 100° give *isobrazileinchlorhydrin* $C_{16}H_{11}O_4{\cdot}Cl$, and isobrazileinbromhydrin $C_{16}H_{11}O_4Br$, and both compounds consist of orange-coloured prisms, which are somewhat readily soluble in water, forming a solution which contains free haloid acid. These interesting substances dye mordanted fabrics colours which are entirely different from those yielded by brazilein, and the shades which are produced especially on calico somewhat resemble those given by alizarin. From these haloid salts by digestion with silver oxide a substance is produced known as *isobrazilein*, which has the formula $C_{16}H_{12}O_6$, but is totally distinct from brazilein.

According to Engels, Perkin, and Robinson (Chem. Soc. Trans. 1908, 93, 1140), whose paper must be consulted for the detailed account of brazilein and its derivatives, these *iso*brazilein salts are derived from 4-3-*indenobenzopyranol* (1), and the sulphate which is *trihydroxy-4-3-indenobenzopyranolanhydrohydrogen sulphate* (2), may be represented thus :



It was found, for instance, that when brazilein trimethyl ether (3) is treated with sulphuric acid, it is converted with loss of methyl alcohol into the dimethyl ether of *iso*brazilein sulphate (4)



These authors assign an orthoquinonoid structure to this and similar oxonium salts.

The *commercial preparations* of Brazilwood known as Brazilwood extract and Brazilwood liquor, are prepared by boiling the ground fresh wood with water, and evaporating the decoction thus obtained to various degrees of consistency without access of air, or as rapidly and at as low a temperature as possible, *e.g.* in vacuum pans.

Dyeing Properties.—Before dyeing, the logs as imported are rasped to a coarse powder, and this is then usually moistened with water and allowed to ferment for some weeks. This operation is performed in order to increase the colouring power of the wood, and there can be little doubt that a considerable quantity of the brazilin present is thereby oxidised to the colouring matter brazilein. It has been considered by some that the fresh wood contains in reality a glucoside of brazilin, which, under the influence of fermentation, is hydrolysed, but no evidence has been forthcoming in support of this suggestion.

Although still used in calico-printing and in wool-dyeing, Brazilwood and its allies have lost much of their importance, chiefly because of the fugitive character of the colours they yield. In calico-printing, sappan liquor is employed for producing steam-reds and pinks, the mordant used being aluminium acetate or stannic oxalate, separately or combined, together with some oxidising agent, *e.g.* potassium chlorate or a copper salt. It also enters into the composition of steam-chocolates and certain steam colours in conjunction with other dyewood extracts. These woods have also been much used in the past along with garancine in dyeing the reds, chocolates, and other colours of cheap prints.

In wool-dyeing these woods have been applied for the purpose of dyeing reds and various shades of claret and brown, the wool being previously mordanted with alum and cream of tartar or oxalic acid, or with potassium dichromate.

in which case other dyewoods, *e.g.* logwood and old fustic, are applied in addition. The colours produced by this method are now only used to a limited extent.

In cotton-dyeing, peachwood-red was formerly obtained by first preparing the cotton with tannin matter, then mordanting with a stannic salt, and finally dyeing with peachwood, sappanwood, &c. Browns were obtained by the use of logwood in addition, with or without a final passage through a ferric salt solution (nitrate of iron). These colours are now replaced by others obtained from coal tar. A. G. P.

BRAZILEIN and **BRAZILIN** *v.* BRAZILWOOD.

BRAZILIAN ANIME *v.* OLEO-RESINS.

BREAD may be defined as the dough made by the mixture of the flour of grain with water, charged in some way with gas so as to distend it, and afterwards baked. The resulting loaf has a delicate spongy structure which causes it to be the most readily and easily digested of all wheat foods. The simplest and most primitive form of bread making consisted merely in mixing flour with water and baking the dough, and it survives still in the Passover cakes of the Jews and in the 'damper' of the Australian settler. The charging with carbonic gas is commonly effected by fermentation with leaven or yeast; alternative methods involve the use of baking powders (*q.v.*) or the direct injection of the gas. In addition to producing gas, fermentation has a profound effect on the constituents of flour, and improves the flavour and digestibility of the loaf.

The mechanical result of aëration is the creation of innumerable vesicles or cells within the dough, which are subsequently distended by heat, the whole mass being encased in the baking within the crust of dextrin formed by the action of heat upon the starch. The making of bread from wheaten flour is only possible because the latter contains gluten. Gluten is a mixture of proteins which becomes viscid when mixed with water, and, when blown up with gas, has sufficient coherence to remain in the form of a honeycomb instead of collapsing and allowing the gas to escape.

Leavening (Lat. *levo*, to rise) has been practised from time immemorial in the East; from the Egyptians it passed to the Greeks and thence to the Romans, whose conquests and colonies extended the art. It consisted in the first instance probably in a natural fermentation of the dough by leaving it to become sour; but to hasten the process it became usual to add to new dough a portion of old fermented paste or 'leaven.' More recently, yeasts were substituted for the piece of leaven. These were of various origin, that from the distillery being the most suitable. To-day, 'pressed' or German yeast, which consists of yeast grown in a special way, purified by repeated washing and compressed into cakes, is the most generally used. This keeps well, is uniform in quality, and enables the baker to exercise a close control over the regularity of the process.

Dough consists roughly by weight of two-thirds flour and one-third water, the quality of the water being a matter of some importance. The softer the water the quicker is the fermentation, and since the quality of the bread depends on fermentation being allowed to proceed to exactly the right point, it cannot be carried out under precisely the same conditions with hard as with soft water.

Chemistry of bread making.—The chief constituents of flour, so far as bread making is concerned, are (1) the carbohydrates, (2) the proteins. The former include sugars and starch, the proteins consist of a small proportion of soluble protein and a large proportion of insoluble gluten.

The gas formed during panary fermentation is produced by the action of the yeast organism on dextrose. Flour contains about 1 p.c. of sucrose and a little raffinose: before fermentation, both these sugars are converted into dextrose by the enzyme *invertase* present in yeast. This amount of sugar would not suffice to give the necessary amount of gas, but it is supplemented by the maltose produced from the starch of the flour, maltose being itself converted into fermentable dextrose by another enzyme *maltase* contained in yeast.

The formation of maltose is effected by the agency of a diastatic enzyme present in flour; it begins directly the flour is wetted and continues throughout fermentation until the loaf is baked. Yeast contains no diastatic enzyme, but it is possible that its action on the proteins of flour facilitates the production of diastase.

Gas escapes from the dough throughout the process of making a loaf, and the supply available must be sufficient to distend the loaf and maintain it fully distended until it is fixed in the oven. Flours which have relatively little diastatic enzyme will produce insufficient gas, and this fact explains perhaps the beneficial results sometimes obtained on adding malt extract, which is rich in diastase, to dough. This question is in reality somewhat more complicated in that diastase consists of two enzymes—a liquefying enzyme which renders the starch soluble, and a hydrolysing enzyme which converts it into maltose. It is the former rather than the latter enzyme which is sometimes lacking in flour.

Gluten is the characteristic and the most important constituent of flour (*v.* GLUTEN). It is the agent which principally determines how much water a dough will take; what length of time it requires to be fermented; what will be the size of the loaves, and their colour, flavour, and general appearance. The baker requires quality rather than quantity: the relation between chemical constitution and quality is not yet fully understood (*see* British Association Report on Wheat, Winnipeg, 1909). During fermentation, gluten becomes softer and at first more elastic, subsequently it softens still further, loses elasticity, and begins to break down. Baker's yeast always contains lactic acid organisms, and the conditions in a long sponge are favourable for the formation of this acid, which has a marked solvent and disintegrating action on gluten. Accordingly, in a long sponge, the gluten is considerably disintegrated. The baker's art consists in taking the sponge when sufficiently mellow. If under-fermented, a foxy crust is obtained; if over-ripe, the gluten becomes too much disintegrated and the loaf is less bulky, inclined to crumble, and in extreme cases becomes sour.

Common salt is very generally added to bread. This is done firstly to give the necessary

flavour, as owing largely to the action of salt in stimulating the palate, minute quantities of other substances can be recognised in its presence. Secondly, salt has a toughening and binding effect on gluten, though it has a solvent effect on some of the proteins of flour. In view of the modern theory that the properties of gluten are due to small quantities of associated salts, the effect of the added sodium chloride must be taken also into account. Salt also checks diastatic action and fermentation to some extent. Use is made of this property by the baker in dealing with sponges which are over-ripe: a little more salt than usual is used in making the dough, and the subsequent fermentation is retarded and the disintegrated gluten somewhat toughened.

To make a large, well-aërated, shapely loaf of good colour and flavour, it is necessary to use a large proportion of flour from strong wheats. Such a flour usually contains more nitrogenous compounds than a weak flour. Commercially, a demand has arisen for strong flours, which accordingly realise a higher price than weak flours. The strongest flours come from parts of the United States and Western Canada, also from Hungary. English wheats give, as a rule, weak flours, which by themselves are unsuited for modern bread making.

It is the object of the large millers to produce a brand of flour suited for bread making which is a blend of several wheats, and to maintain this brand of flour of uniform quality throughout the year. The preparation of sample loaves, made under carefully standardised scientific conditions, still remains the most satisfactory test of quality, and many flour mills maintain a laboratory for this purpose.

According to Humphries, the starch of flours made from wheat grown in hot, dry climates is very stable and resists disintegration. Such flours require special treatment, the addition of malt extract being a very common process. This addition generally causes an improvement in flavour, due, it is supposed, to the production of dextrinous products, which further have the effect of making the bread more moist.

There is a loss of weight during panary fermentation, due to the conversion of carbohydrates into alcohol and carbon dioxide. Jago estimates this loss at 1·3 p.c.; other authorities give somewhat higher values. Experiments made at Pittsburg indicate that over two-thirds of the total fat present in flour is lost during baking.

The manufacture of bread. To-day, in large towns, bread is usually made in bakeries on a manufacturing scale, and machinery is employed for the mixing of the dough, weighing and moulding of the loaves, whilst the baking is carried out in large draw-plate ovens.

There are various systems of bread making depending on whether the dough is made right off in one operation, or whether a portion of the flour, the yeast and the water, are first made up into a loose paste—the sponge—and the rest of the flour added some hours later. A third system involves the preparation of a ferment most commonly consisting of potatoes, boiled and mashed with water to which a little raw flour is added. The yeast is introduced into this and fermentation carried out so as to favour growth and reproduction and get the yeast in a particularly active state. Flour is added to make a sponge, and this, some hours later, made into dough. The longest system of fermentation is that practised in Scotland. An eighth or tenth of the flour is made into a fairly tight dough with a little yeast and allowed to lie 14 to 18 hours, during which time the gluten becomes almost entirely soluble, and the dough acquires a distinctly vinous smell and taste. It is then broken up with flour and the remainder of the liquor to a thin sponge, which lies about 1½ hours till it shows signs of turning and is then made up into a rather soft dough. The long systems formerly in use, were partly the result of custom and partly due to the slow working yeasts used. To-day, particularly in large bakeries, the tendency is in the direction of the straight dough, though the sponge-and-dough method is very largely practised. It has been claimed that the longer processes require less yeast, make bulkier bread, and bread of better flavour.

When the dough is ready it is scaled off and kneaded into shape. This presses out nearly all the gas and toughens the gluten; if it is not thoroughly done the loaf is likely to contain holes. The loaves are next put aside in a warm place to prove, during which the gluten relaxes and the yeast expands the dough evenly. Too much proof must be avoided, as on putting the bread in the oven the excessive expansion is frequently followed by the collapse and flattening of the loaves. The loaves are then baked at 450°–500°F., a 2-lb. loaf requiring about 40–50 minutes. During baking, the gases are at first expanded and the dough swells, the yeast is killed, some of the starch cells burst, the heat sets the gluten and the starch, and finally the crust is converted into dextrin and in part caramelised.

It is the baker's object to get the maximum number of loaves from a sack of flour. Accordingly, that flour is selected which has the greatest power to take up and retain moisture. Such flours are often termed strong. A sack (280 lbs.) of good flour yields about 96 quartern loaves.

Vienna bread is a term applied to rolls and light fancy bread baked in an atmosphere entirely charged with steam, to obtain which a special oven construction is adopted. The starch of the flour is burst by heat and changed into dextrin by the aid of moisture, so that a rich golden-brown highly glazed crust is obtained.

Leavened bread.—In France and elsewhere on the Continent, bread is made from leaven, but in the more important towns this mode of bread making has been given up for the Viennese and English processes. The practice in the preparation of the leaven consisted in a series of stages ('levain de chef, levain de première, levain de seconde, levain de tout point'), by which, starting with a piece of dough put away from a previous baking and adding at intervals more and more flour and water, the required quantity is leavened. From this is taken a half, which when baked yields a dark, sour bread; the remainder, being again mixed with a quantity of flour and some yeast, produces a whiter and less sour dough, a portion of which is baked and the residue once more added to fresh flour. This subdivision is repeated three times, the bread improving at each

stage. A characteristic example of leavened bread is seen in the rye bread (Schwarzbrod) of Germany.

Next to wheat, rye is the chief bread-making grain throughout the world, and in particular it is largely used in Northern Europe. Rye bread is moister, closer, and darker in colour than ordinary household bread. There are several qualities, differing in the proportion of bran contained, the so-called 'pumpernickel' being an extreme example. Fine rye bread is as digestible as wheaten bread, but in the case of pumpernickel a very large proportion is unabsorbed (Romberg, Archiv. f. Hygiene, 1897, 28, 244).

Baking Powders.—Carbon dioxide may also be generated within dough by the action of baking powders, which are usually mixtures of sodium carbonate and some acid or acid salt, and evolve gas when moistened or heated. Owing possibly to the difficulties of distributing fresh yeast, baking powders were formerly widely employed in America. They are not used much in this country for white bread. They are usually classified according to the acid constituent, as tartrate, phosphate, or alum powders (*v.* BAKING POWDERS). The so-called self-raising flour contains baking powder already mixed with it.

Aërated bread is made by injecting carbon dioxide into dough by mechanical means. The process was originated by Dr. Dauglish in 1859, and at one time enjoyed considerable popularity, but it has not met with universal favour on account of the raw and insipid taste of the bread, due to the absence of the products which yeast produces during fermentation. The carbon dioxide is produced separately and forced into water under pressure: this water is mixed with the flour in a specially constructed vessel, in which the pressure is maintained. On opening the vessel, the dough rises and can be immediately baked. The advantages claimed for the system are uniformity of result, and the avoidance of the losses in weight which occur during fermentation. A later development consisted in mixing a little wort, made from malt and flour and fermented till sour, with the water to be aërated, so as to improve the flavour. The process is eminently suited for the manufacture of whole-meal bread, as the preparation of a batch of dough can be effected in thirty minutes.

Composition of Bread.—The general composition of bread is very variable. About two-thirds of the volume is made up of gas. By weight it contains 40–50 p.c. of water and 6·5 p.c. of protein, the balance being mainly carbohydrate. Hutchison gives the following mean figures for a number of breads analysed by him:—

	Water	Protein	Fat	Carbohydrates	Cellulose	Ash
White .	40	6·5	1·0	51·2	0·3	1·0
Whole meal .	45	6·3	1·2	44·8	1·5	1·2

On keeping, a loaf gradually loses moisture to the extent of 8 p.c. in 48 hours, 14 p.c. in 72 hours (Goodfellow) or 14 p.c. in 1 week (v. Bibra). At the same time, the bread becomes stale, but this change is not attributed to loss of moisture, as much of the freshness is restored on heating, during which considerably more water is lost. It is suggested that staleness is due to a gradual combination of water with the starch or gluten which is readily broken up by heat; or, alternatively, that it is due to the shrinkage of the fibres which form the walls of its visible pores.

The adulteration of bread with alum, zinc, and copper sulphates, lime, &c., is now entirely a thing of the past. These were added to prevent the injurious effects of an excess of diastase on the starch during panary fermentation when inferior flour was employed. The cheapening of flour and the critical demands of the public for a well-risen white loaf, as well as improvements in the miller's technique, have necessitated the use of the best flours in bread.

The question of colour, meaning brightness of appearance in crumb and crust, is an important one; at the moment, the demand is for a white loaf. Colour is largely a question of optics; a weak but very white flour may make poor dingy-looking loaves, whilst a darker, stronger flour will make loaves which are better aërated and hence appear much whiter.

A modern development is the artificial bleaching of flour, usually with nitrous fumes produced by some electrical process. There is no proof that bread made with bleached flour is deleterious to health, but its use has been forbidden in America under the Pure Food Laws. It is a matter of controversy whether bleaching by nitrogen peroxide is due to oxidation or to nitration. Bleaching does not change a low-grade flour into a higher one, and bleached flour should therefore be declared as such.

The souring of bread is one of the baker's problems. It is the result of a combination of bacterial fermentations, the bacteria being introduced by the yeast, by the flour, or, as should not occur, by the use of dirty vessels. The flavour of fermented bread improves gradually as the process proceeds until a maximum is reached, after which, if fermentation is continued, it begins to deteriorate. At this stage the alcoholic ferment is exhausted and the acid fermentation begins to predominate. The sourness is mainly due to lactic and acetic acids, the odour to acetic and sometimes butyric acids.

Such bread-diseases as ropiness (compare E. J. Watkins, Ropiness in Flour and Bread, J. Soc. Chem. Ind. 1906, 350) are due to specific bacteria.

In a modern bakehouse, bacterial diseases should not occur; they may often be traced to the use of unsound flour.

Whole-meal Breads.—The majority of the patent breads belong to the 'brown' variety, and contain more of the wheat grain than the white flour. In some, the finely ground bran is introduced, in others the germ, whilst a third class claim to contain the complete wheat grain. Bran is very rich in diastatic enzyme, here termed cerealin, and its introduction causes a very rapid conversion of the starch into dextrin and sugar. This causes the dough to become soft and clammy and to bake brown: in addition, it becomes very prone to souring. The use of sodium bicarbonate and hydrochloric acid for aërating whole-meal bread is common. When the fermentation process is used, the bran is not introduced until the dough stage. Whole-meal bread has a great tendency to become sodden; it has to be baked for a considerable time, and consequently often has a thick crust. Germ has a very injurious effect on flour, owing to its

diastatic character, and the tendency to become rancid. Every effort is therefore made to remove it as completely as possible. When subjected to the action of superheated steam, the germ is cooked, the diastatic properties are destroyed, and it acquires a pleasant malt-like, nutty flavour and aroma. This process was patented by R. Smith of Macclesfield, and a mixture of one part of treated germ and three parts of white flour constitutes Hovis flour, from which Hovis bread is made.

The relative nutritive values of white and whole-meal bread is a highly controversial subject. It is claimed that whole-meal bread is richer in protein and so more valuable, but this is far from being generally true. A second contention is the larger amount of mineral matter, especially phosphoric acid, in the brown bread. This is certainly true, but experience has shown that the mineral matter is not all absorbed from white bread, whilst in whole-meal bread the quantity absorbed is so much less that it is probable the blood obtains much the same amount from both (Hutchison). Whole-meal bread is defectively absorbed, owing to the cellulose which it contains preventing the gastric juices from gaining access to the neighbouring nutritive ingredients, and for the same reason it interferes somewhat with the absorption of other foods. When the unsatisfactory nature of the whole-meal bread itself and the precautions necessary in its manufacture are taken into consideration, it is to be deplored that a section of the public should demand bread in this form. With bread containing added germ the case is different, the bran is absent and the food value, both as regards protein and phosphate, is larger than of white bread.

The use of flour containing the untreated original germ of the wheat berry for bread is disadvantageous, since the flour easily becomes rancid and the germ enzymes commence to act on the gluten from the moment the flour is made, causing the loaf to be of poor colour and to be less finely vesiculated and digestible. These factors more than outweigh the advantages of the very small additional amounts of protein and phosphate introduced and the slightly sweeter flavour of germ bread.

The desire for more phosphates can be met by the addition of phosphoric acid to the flour, as is indeed being done at the present moment during the milling process in order to improve the quality of flour (compare Humphries, Eng. Pat. 13135 and 17279 of 1908; Chitty and Jago, Eng. Pat. 22434 of 1909; Levin, Eng. Pat. 3673 of 1910).

Authorities.—Jago, Science and Art of Breadmaking, London, 1911; Hutchison, Food and the Principles of Dietetics, London, 1911; *Wheat*: Brit. Ass. Report, Winnipeg, 1909; Hamill, Local Govt. Board, No. 114, 1911.

E. F. A.

BREAD FRUIT. The fruit of *Artocarpus incisa* (Linn.). The tree grows freely in tropical islands, and yields fruit continuously for 9 months in the year. The fruit is nearly spherical, and sometimes weighs 5 or 6 lbs. It is usually gathered while yet unripe, *i.e.* before its starch has changed into sugar; sometimes the unripe fruit is peeled, wrapped in leaves and cooked whole, when a product resembling ordinary bread is obtained, or the unripe fruit is dried, powdered, and sifted, yielding a flour which has the following composition:—

Water	Protein	Fat	Starch	Fibre	Ash
14·3	1·0	0·2	83·8	0·2	0·4

(Balland, J. Pharm. Chim. 1903, 17, [10] 476).

The leaves and wood of *Artocarpus incisa* are devoid of colouring matter (A. G. Perkin, Chem. Soc. Trans. 1898, 73, 1019). A closely related tree (*Artocarpus integrifolia*) bears a still larger fruit, 'jak fruit,' weighing about 25 lbs., of which about 26 p.c. is flesh, the remainder being rind 66 p.c., and seed 8 p.c. The flesh, when ripe, contains about 5 p.c. of sugar, mainly cane sugar (Prinsen Geerligs, Chem. Zeit. 1897, 21, [72] 719).

H. I.

BREAN *v.* OLEO-RESINS.

BREEZES. (*Braise*, Fr.) The dust of coke or charcoal. The coke burner applies this term to the small residual coke obtained in coke burning. The sifted ashes removed from houses is called 'breeze,' and sold under that name to brickmakers and others. An arrangement for burning breeze is described in J. Soc. Chem. Ind. 5, 425.

BREÏDIN, BREÏN *v.* OLEO-RESINS.

BREMEN BLUE and **BREMEN GREEN.** Pigments containing a basic copper carbonate with alumina and calcium carbonate.

BREWING. 1. *Introduction.* Beer (Fr. *bière*; Ger. *bier*) may be defined as a spirituous liquor made from any farinaceous grain, but preferably from barley, which is first caused to germinate, then ground and mashed with hot water, whereby its fermentable substance is extracted. This wort, as it is then termed, is next boiled up with hops, which, besides imparting an agreeable bitterness to it, precipitates certain albuminous bodies. The liquor drained off from the hops is cooled down, yeast added, and fermentation set up. After the liquor has ceased fermenting it is freed from the yeast, run off into casks and sent away for consumption. It may be of different degrees of strength and colour, according to the quantity and nature of the ingredients employed in its manufacture; thus we may have mild ale, strong ale, light dinner ale, pale ale, bitter beer, porter, and stout.

2. The ingredients used in the manufacture of English beer are water, barley malt, malt adjuncts such as maize, rice, sugar, glucose, saccharum, &c., hops, and yeast.

3. **Water.** The principal seat of the brewing trade in Great Britain is Burton-on-Trent, which owes its great commercial prosperity in this branch of chemical industry to a certain chemical property possessed by the waters of this locality, which render them pre-eminently suitable for brewing purposes. This property is nothing more or less than the presence of calcium sulphate in large quantities in these waters, derived from the deposits of gypsum contained in the Keuper marls of the district.

4. The waters supplying the Burton breweries are derived from two sources: (1) from the valley gravels (shallow wells), and (2) from the red marls and water stones of the new red sandstone formation, obtained by artesian borings.

The following analyses of these waters may be regarded as typical. No. 1 sample, from a well sunk to the depth of 29 feet in the valley

gravels, very fairly represents the composition of the mineral constituents of the older and shallow wells of the district, in which the sulphates of lime and magnesia are partially replaced by carbonates of the same metals due to the percolation of rain water charged with carbonic acid gas

TABLE I.

—	In grains per Imperial gallon	
	Shallow well	Deep well
Calcium sulphate .	25·480	70·994
Magnesium sulphate	Absent	12·600
Calcium carbonate .	18·060	9·046
Magnesium carbonate	9·100	5·880
Potassium sulphate .	2·275	0·696
Sodium sulphate .	7·630	18·300
Sodium chloride .	10·010	9·120
Ferric oxide . .	0·837	1·130
Silica . . .	0·840	1·120
Total mineral matter	74·232	124·206

through the gravel bed. No. 2, from an artesian boring sunk *through* the gravel and *into* the underlying red marl to a total depth of 97 feet, may be taken as a type of the deep wells of the district.

It will be seen from these tables that the chief characteristics of both waters are the large quantities they contain of certain mineral salts, but especially of gypsum. The brewing excellences of the Burton water are supposed to arise partly from its freedom from organic matter, but mainly from the circumstance that the mineral constituents are of such a nature as to favour the extraction of all the alcoholic principle of the malt without at the same time taking up the colouring matter; hence the Burton water is peculiarly fitted for brewing those various qualities of pale ale for which the town has been so long celebrated.

5. From this it will be seen that no matter how pure a water may appear to be by chemical analysis, it by no means follows that such a water would be the most suitable for brewing purposes or produce the best beer. Certainly it is advisable that a brewing water should contain in solution as little as possible of those matters which are derived from the decomposition of organic substances, and especially those of animal origin, but at the same time, unless it holds in solution certain mineral salts in given quantity it is comparatively useless for brewing purposes. Of course, the presence or absence of such salts will entirely depend on the geological nature of the various strata throughout the country; thus, whilst the Burton waters are highly saline, the waters of Thames Valley deep wells are strongly alkaline, whilst in Wales, Cornwall, and Cumberland we find waters containing little or almost no solid matter in solution, or frequently highly peaty in character and containing as much as 4 grains per gallon of organic matter, but entirely of vegetable origin.

6. For purposes of convenience, all waters may be classified as follows:—

I. Alkaline, from the chalk, the predominating mineral constituents being potassium and sodium carbonates.

II. Calcareous, from the carboniferous and liassic limestones, the predominating constituents being calcium and magnesium carbonates.

III. Saline (*a*) from the new red sandstone, the predominating constituents being calcium and magnesium sulphates.

IV. Saline (*b*) from wells near the coast, the predominating constituent being sodium chloride.

V. Peaty, containing principally vegetable organic matter.

VI. Waters from the primary rocks, containing very little or only traces of mineral matters in solution.

VII. Waters of no distinctive character.

The following analyses may be given as examples of these various types of water:—

TABLE II.

—	1	2	3	4	5	6	7	8	9
	Alkaline	Calcareous	Saline (*a*)	Saline (*b*)	Peaty	Primary rocks	No distinctive character	Mild ale	Pale ale
Calcium sulphate . . .	—	0·69	70·99	6·39	2·25	0·22	1·53	25	40
Magnesium sulphate . .	—	—	12·60	0·48	2·77	—	—	5	8
Calcium carbonate . .	3·25	13·87	9·04	—	—	—	1·27	15	15
Magnesium carbonate . .	1·47	0·44	5·88	4·87	0·87	—	1·35	—	—
Potassium sulphate. . .	7·31	—	0·97	—	—	—	—	5	10
Sodium sulphate . . .	—	—	13·30	—	—	—	—	—	—
Potassium carbonate . .	9·58	—	—	—	—	—	—	—	—
Sodium carbonate . . .	6·61	—	—	—	—	—	—	—	—
Calcium and magnesium nitrates	—	—	—	—	—	—	0·46	—	—
Potassium nitrate . . .	—	—	—	—	0·68	—	0·27	—	—
Magnesium chloride . .	—	—	—	—	—	—	—	3	5
Potassium chloride . .	—	—	—	—	0·79	—	0·48	—	—
Sodium chloride . . .	14·99	1·73	9·17	59·67	1·45	1·53	1·76	20	30
Oxides of iron and alumina .	0·03	0·45	1·13	0·35	0·84	—	0·10	—	—
Silica	0·33	—	1·12	0·28	0·49	0·40	0·33	—	—
Total mineral matters . .	43·62	17·18	124·20	72·04	10·14	2·15	7·55	—	—

7. From the foregoing it will be seen that for the brewing of ales the water to be most preferred is undoubtedly that of the saline type, and if it should fall to the brewer's lot not to possess such a water supply he must render the one he has available by the addition of certain saline ingredients suitable for his purpose. In order to do this a complete analysis of the

mineral constituents of the water must first be made, and then sulphates of lime, magnesia, and potash, and sodium chloride added in such proportions as to bring the mineral constituents up to the required standard, either to that shown in column 8 if intended for mild ales, or to that of column 9 if intended for pale ales.

In the case of neutral waters, the necessary mineral salts are simply added to the water in the given proportions, but if the water be alkaline, the alkaline carbonates must first be destroyed before further treatment. An essential condition in hardening a water with calcium sulphate is that the process shall be regular, and the best method of getting the gypsum into solution is decidedly by passing the water as it issues from the supply tap or storage cistern through a tank filled to three quarters its depth with gypsum stones about the size of a hen's egg. The method of procedure is shown below:—

A is a wooden round, having a perforated false bottom B, on which the gypsum stones rest; C, water inlet from main or cistern; D, indicating valve; E, waste-pipe having a fall of 30 feet for washing out; F, wash-out valve; G, overflow pipe to liquor tank. The valve D being opened to the requisite degree, and F closed, the water enters at C, percolates through the gypsum in A, and flows over through the pipe G into a liquor tank. The rate of flow of the water which determines the amount of gypsum to be taken up is regulated by the valve D. The size of gypsum tank and the speed at which the water passes through will determine the quantity taken up. As a rule, a tank capable of holding about a ton of gypsum and with a water of the composition of No. 2 flowing through it at the rate of three barrels per minute, takes up about 20 grains per gallon of calcium sulphate. Fresh gypsum must be added daily so as to keep the depth of layer of gypsum as regular as possible. To prevent an accumulation of slimy deposit which always takes place to a greater or less extent, the gypsum in the tank should be thoroughly well washed every other week; this may be done by closing D and opening F, then turning water on at the top of A, this passing through such a length of pipe as E causes a certain amount of suction which produces the desired cleansing effect. Some brewers recommend the addition of the gypsum in a state of fine powder either to the hot liquor tank before, during, or after the heating of the water preparatory to mashing, others sprinkle it over the grist as it runs into the mash tun, whilst others again add it to the wort as it is boiling up in the copper. None of these methods can be recommended, as in no one case will the *whole* of the gypsum be taken into solution, hence the brewing liquor will, according to varying circumstances, contain different quantities of calcium sulphate, but always less than is really required. After the whole of the water required for mashing and sparging has run through the gypsum tank into the hot liquor back, then the other salts are added. This may be most conveniently accomplished by the use of kainite and common salt in such proportions as chemical analysis may point out to be necessary.[1] For instance, let us take water No. 4; here it was found that by passing the natural water through about a ton of gypsum at a speed of three barrels per minute, 20 grains per gallon of calcium sulphate were taken into solution; kainite at the rate of 2 oz. per barrel and common salt 1 oz. per barrel were next added; the mineral constituents of this water had then the composition shown in column II.

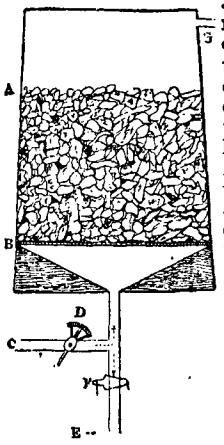


FIG. 1.

On referring to our table of typical analyses, it will be seen that this water is of the mild ale type. To render it suitable for brewing pale ales, the water must be run at less speed through the gypsum tank so as to increase the calcium sulphate, and further quantities of kainite and common salt must be added as shown in column III.

TABLE III.

—	I.	II.	III.
Calcium sulphate	0·69	20·69	35·69
Magnesium sulphate	None	4·41	8·82
Calcium carbonate	13·87	13·87	13·87
Magnesium carbonate	0·44	0·44	0·44
Potassium sulphate	None	5·23	10·46
Magnesium chloride	None	2·88	5·76
Sodium chloride	1·73	18·35	32·96
Oxides of iron and alumina	0·45	0·45	0·45
Silica	None	—	—
Total solid matters	17·18	66·32	108·45

In the case of alkaline waters, as soon as the calcium sulphate enters into solution a distinct chemical action between it and the alkaline carbonates takes place, calcium carbonate being formed, and sulphates of the alkalis. It is generally assumed that this reaction takes place according to the equation

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

but this has been proved not to be the case. From numerous experiments made to determine this point, the following conclusions were arrived at:—

(*a*) If the quantity of calcium sulphate added be less than the quantities of alkaline carbonates present, then *all* the calcium sulphate is at once converted into calcium carbonate, and an equivalent quantity of alkaline carbonates is converted into alkaline sulphates.

(*b*) If the quantity of calcium sulphate added

[1] Analysis of kainite:

Magnesium sulphate	17·92
Potassium sulphate	24·79
Magnesium chloride	12·35
Sodium chloride	29·20
Water	15·74
	100·00

be equivalent to the quantity of alkaline carbonates present, then only about three-fourths of the calcium sulphate is converted into calcium carbonate, and an equivalent quantity, that is to say, three-fourths of the alkaline carbonates present, is converted into alkaline sulphates. As we increase the calcium sulphate, the alkaline carbonates decrease, until when we add double the equivalent of calcium sulphate nearly the whole of the alkaline carbonates is converted into alkaline sulphates.

(c) The last portions of the alkaline carbonates seem to be very persistent, for not until we increase the quantity of calcium sulphate to nearly three times the quantity of alkaline carbonates originally present do we find that the last traces of these substances finally disappear. These are the results of numerous experiments carried out by the author both in the laboratory and on the large scale in breweries where the deep-well water supply was highly alkaline in character, and it was found that the results obtained on the large scale fully confirmed those arrived at in the laboratory.

The following analyses of an alkaline water before and after treatment with gypsum will make this more clear :—

ANALYSES OF AN ALKALINE WATER BEFORE AND AFTER TREATMENT.

—	1 Before	2 After gypsum	3 After gypsum	4 After gypsum and $MgCl_2$
Calcium sulphate	absent	27·92	35·62	44·95
Magnesium sulphate	absent	absent	absent	14·39=11·39 ($MgCl_2$)
Calcium carbonate	3·25	13·44	16·42	16·42
Magnesium carbonate	1·47	1·47	1·47	1·47
Potassium sulphate	7·31	14·21	19·39	9·39
Sodium sulphate	absent	8·86	8·86	absent
Potassium carbonate	9·58	4·11	absent	absent
Sodium carbonate	6·61	absent	absent	absent
Potassium chloride	absent	absent	absent	8·56
Sodium chloride	14·99	14·99	14·99	22·29
Oxides of iron and aluminium	0·03	0·03	0·03	0·03
Silica	0·38	0·38	0·38	0·38
Total mineral matter	43·62	85·41	97·16	117·88

Column 1 shows the composition of the mineral constituents of the natural water.

Column 2, the same water after 41·79 grains per gallon of gypsum had been added, but the water was found to be still alkaline, and not until 53·54 grains of gypsum were added did the alkalinity disappear.

Column 4 gives the composition of the mineral constituents after the addition of a further quantity of gypsum, and 11·39 grains of magnesium chloride to decompose the excess of alkaline sulphates.

The ales brewed with this water after the above treatment were found to give every satisfaction, and to compare very favourably with the best Burton pale ales.

It will be noted that the alkaline sulphates originally present in the water are considerably increased by such treatment, and, as a large excess of these substances exercises a decidedly injurious effect both in mash tun and copper, it is advisable to get rid of this excess by adding sufficient quantity of calcium chloride or magnesium chloride to the water, whereby a portion of the alkaline sulphates is converted into alkaline chlorides, the calcium or magnesium chlorides being at the same time changed into sulphates. We thus get a water highly saline in character and possessing all the properties of a typical Burton water suitable in every way for pale-ale brewing.

Having once ascertained the exact quantity of gypsum required to be added to the water, either for the purpose of increasing the permanent hardness or for the destruction of the alkaline carbonates, it is very easy for the brewer to keep a check upon his gypsuming process as follows: In the case of non-alkaline natural waters, the total hardness of the water is determined, and the same after the water has been hardened. The first subtracted from the latter gives the hardness expressed as degrees of calcium carbonate (1° being equal to 1 grain of calcium carbonate per gallon) due to the gypsum dissolved; this multiplied by the factor 1·36 will give the grains per gallon of calcium sulphate taken up during the process of gypsuming. This method answers admirably for all practical purposes, the error as compared with direct analysis not varying more than about ½ grain per gallon. For example:

Non-alkaline water (*v. Analysis* No. 4).

Total hardness before gypsuming		12·6
" " after "		27·44
27·44—12·6=14·84, which multiplied by 1·36=	20·99	
$CaSO_4$ found by direct analysis	21·23	
	Diff.	0·24 of a grain

In the case of alkaline waters the total hardness of the natural water is determined as before; then having found by trial the quantity of $CaSO_4$ necessary for the destruction of the alkaline carbonates and for the permanent hardness, the water is run through the gypsum tank at

such a speed as to take up this quantity of $CaSO_4$. As soon as the requisite amount has run through, the total hardness of the treated water is determined. The amount of calcium sulphate in the water is next ascertained by chemical analysis, and the figures thus obtained taken as standards of comparison for all subsequent determinations. Thus an alkaline water containing 16·19 grains per gallon of alkaline carbonates, after hardening was found to have taken up 55·42 grains per gallon of calcium sulphate. Of this 17·92 grains were required to convert the alkaline carbonates into sulphates, leaving 37·5 grains of available $CaSO_4$.

The total hardness of this water was 43·75. Hence 43·75° of hardness correspond to 37·5 grains $CaSO_4$. Another determination of total hardness of this water after gypsuming was made some weeks later; this was found to be 45·5. Therefore

$$\frac{45{\cdot}5 \times 37{\cdot}5}{43{\cdot}75} = 39 \text{ grains of available } CaSO_4.$$

This does not give such accurate results as in the case of neutral waters, but is quite near enough for all practical purposes.

Treatment of water for brewing black beers, stout and porter.—It is a well-known fact that the best stout and porter are brewed in London and Dublin. Dublin waters are exceedingly soft, whilst London water is strongly alkaline, *i.e.* it contains alkaline carbonates, and although containing as much as from 40 to 50 grains per gallon upon the average of total solids, these London deep-well waters are yet comparatively soft, showing only 5° of hardness with the soap test. From this it will be seen that one of the necessary conditions for the successful production of black beers is, *primâ facie*, a soft water. Hence, a brewer whose water supply contains large quantities of magnesium and calcium sulphates, *i.e.* a hard water like the Burton waters, cannot expect successfully to brew black beers, but must fall back upon the town supply if that is of only a moderate degree of hardness. In the case of naturally soft waters, such as a London or Dublin water, no further treatment is necessary, but in the case of a non-alkaline water, such a water should first be well boiled so as to precipitate the $CaCO_3$, then, whilst still boiling, Na_2CO_3 at the rate of 10 grains per gallon and 30 grains of NaCl per gallon should be added to the brewing liquor, the whole well mixed up and then allowed to stand until the $CaCO_3$ has completely subsided, and the mash proceeded with as usual.

8. Having glanced briefly at the composition of various types of water and the advantages or disadvantages they possess from the point of view of the brewer, we now proceed to consider the relative effects produced on the malt wort by the several mineral constituents usually found to occur in water.

As has been seen from the tables of analysis on page 527, the quantity and character of the various mineral substances found in natural waters vary considerably, and depend on the nature of the rocks through which the water percolates. An interesting series of analyses of water from the different geological formations of England was made by Sir Edward Frankland, and published by him in his work on Water Analysis, to which the reader is referred.

The most frequently occurring substance in solution in natural waters is calcium carbonate, associated to a greater or less extent with magnesium carbonate. These carbonates are held in solution by the carbonic acid which is always present in natural waters; they probably exist in solution as bicarbonates. On boiling, this excess of carbonic acid is driven off, and the calcium and magnesium carbonates are precipitated. There is no doubt that these carbonates play a very important part in the brewing economy. Although a large portion of these salts is thrown out of solution during the heating of the water preparatory to mashing, yet the greater part of the precipitated carbonates remaining in suspension finds its way into the mash tun, and there combines with certain organic acids, principally lactic acid, always present in malt, forming soluble salts. This neutralisation of at least a portion of these organic acids must exert an important influence on the various processes which take place subsequently.

The amount of calcium and magnesium carbonates varies considerably, but 12–15 grains per gallon may be taken as a fair average. It is usual in those breweries where the waters contain very little or none of these salts to sprinkle calcium carbonate or chalk through the grist as it goes into the mash tun at the rate of 4 oz. per quarter of malt (about 10 grains per gallon of water).

Calcium sulphate occurs less frequently than the carbonate, but, with the exception of sodium chloride, exercises a more important influence on the mashing and boiling processes than any of the other salts present in natural waters.

A very interesting article on this subject by Southby appeared in the Country Brewer's Gazette for 1879, in which he proves very conclusively that, contrary to the opinion prevalent among brewers, calcium and magnesium sulphates, even when present in the brewing water in very large proportions, have no appreciable effect on the solubility of the nitrogenous matters of malt; their principal effect in the earliest stage of brewing operations is to greatly facilitate the ultimate fining of the beer by causing those matters which are rendered insoluble by boiling to separate in a flocculent form instead of in that minute state of division which results in the beer remaining obstinately cloudy, as so many brewers find to their cost. In addition to this, calcium sulphate possesses a decided antiseptic action, as worts brewed with a sulphated water resist the action of the fermentative germs when exposed to the atmosphere better than those brewed with a softer water. The presence of calcium sulphates in a wort also prevents the solution of the coarser bitter principles of the hop, hence a brewer employing a sulphated water can use a much larger proportion of hops, if necessary, without rendering his ales excessively bitter. The same applies to magnesium sulphate. Valuable as the above sulphates are in the production of pale and mild ales, they are absolutely injurious in the brewing of porter and stout if present to the extent of more than 3 grains per gallon.

These results have been confirmed by Moritz and Hartley (Brewer's J. 1883, 92); they find, however, that these sulphates extract more nitrogenous matter from malt than any other

of the mineral constituents of water do, and Matthews (B. T. R. 1887, 295) is of opinion that these nitrogenous substances are of the nature of coagulable albuminoids. We must at the same time not forget that, by using a water containing appreciable quantities of calcium sulphate in solution, a large proportion, if not all, of the phosphoric acid existing in the malt, probably as potassium phosphate, is by double decomposition converted into acid calcium phosphate. It is well known that this substance exercises a powerful influence on certain albuminoid substances, especially at high temperatures. Hence the precipitation in flocks of these bodies, when the wort is boiled in the copper, is no doubt due in great measure to the action of this salt.

Water containing alkaline carbonates must undoubtedly be condemned as unsuitable for brewing mild or pale ales. It is well known that certain nitrogenous matters, whose presence in malt wort would have a most injurious effect, are freely soluble in slightly alkaline waters; these remain unchanged during the process of fermentation, and render the finished beer persistently cloudy, besides forming a suitable nidus for the development of various forms of bacteria. A large amount of colouring matter is also extracted from the malt by alkaline waters, whilst the diastatic action is considerably impeded; in the copper also certain resinous matters are extracted from the hops, which impart a bitter and rank flavour to the finished beer.

Alkaline sulphates if present in excess (more than 10 grains per gallon) have the same action, though in a very much diminished degree, as alkaline carbonates, more especially sodium sulphate. Potassium sulphate, on the other hand, if present to the extent of not more than 6 to 10 grains per gallon, has a decidedly beneficial effect, acting much in the same manner as magnesium sulphate.

Calcium chloride gives to the beer a harsh, coarse flavour.

Magnesium chloride, if present in small quantity, 2 to 4 grains per gallon, is supposed to be beneficial to fermentation.

With regard to the beneficial influence of sodium chloride in a brewing water, there can be no question whatsoever. Some of the finest ales in the United Kingdom are brewed in districts where sodium chloride occurs in the natural well waters to a larger extent than is allowed by excise regulations to be present in the finished beer.

Alkaline chlorides add considerably to the palatefulness of the finished beer, exercise considerable antiseptic properties during fermentation, and contribute to a general mellowness and roundness of flavour which without them is absent in the best brewed ales, mild or pale.

The question of nitrates is still a mixed one; the balance of evidence seems to be that where they are not derived from recent sewage contamination their presence in small quantities acts as a stimulus to fermentation, but a water containing more than 4 grains per gallon of potassium nitrate ought to be looked upon with grave suspicion, if not altogether condemned for brewing purposes, more especially as it is impossible to get rid of nitrates once they are found to be present in water. Nevertheless, the fact remains that in several breweries where nitrated waters are used for brewing, the yeast keeps clean and vigorous and the ales are all that can be desired; but it is only fair to state that in such breweries sugar to the extent of at least one-fifth the quantity of malt is also used.

Iron in any shape or form is most injurious, but as it exists mostly in natural waters in the form of carbonate, it can be converted by oxidation into the insoluble peroxide and removed by subsidence or filtration.

The organic matter in water may be of two kinds, vegetable and animal; the vegetable organic matter is mostly of peaty origin, and as such cannot form suitable pabulum for bacteria, and first-class mild and light ales have been brewed from peaty waters after treatment with gypsum and kainite; but on the other hand, where the organic matter is of animal origin, derived from sewage contamination containing such matter in solution, as it necessarily must be, the water, on biological examination, will in all probability be found to be highly contaminated with disease germs; and although all of these germs as well as their spores are most unquestionably killed during the boiling of the wort in the copper, still such a water must be regarded as a dangerous one to use for brewing purposes as indicating the presence of matter in solution which neither boiling nor filtration can destroy or modify, and which at the first moment that favourable circumstances present themselves will serve to nourish and promote the growth of such germs of disease as may find their way subsequently into the beer or wort brewed from such a water.

9. Barley. The grain which for centuries has been most generally acknowledged to be best adapted for brewing purposes is barley. Of this cereal as many as 100 varieties have been cultivated in this country at one time or another, but the one most generally preferred by brewers is the narrow-eared, two-rowed type generally known as the 'Chevalier' (*Hordeum distichum*). Several varieties of Chevalier barley are grown in some parts of the country, and give good results, *e.g.* Archer 'Stiff Straw.' There is also another type of the two-rowed barley known as Goldthorpe, which has been malted in increasing quantity for some years, and often gives excellent results. This barley, having a stouter straw than Chevalier, is able to withstand bad-weather conditions better.

The various species of cultivated barley are distinguished as two-rowed, four-rowed, and six-rowed, according to the number of fertile spikelets on the ear. The first and last of these species are the most characteristic, the first including the finest varieties of English barley.

The different varieties have been classified by E. S. Beaven as follows (J. Inst. Brewing, 1902, 8, 547):—

Hordeum distichum.—Commonly known as six-rowed barley, ear wide, short distance between the corns. Grown in England as a winter sort. Found in Chilian brewing barley.

Hordeum vulgare.—Known as four-rowed, ear narrow, long distance between the corns. The 'bere' or 'bigg' of Scotland is of this variety as well as most 'Light Foreign.'

Hordeum zeocriton.—Two-rowed barley, ear

wide, comparatively short distance between the corns. The Goldthorpe barleys are of this type.

Hordeum distichum.—Two-rowed barleys, ear narrow, comparatively long distance between the corns. The Chevalier barleys are of this type, as well as many long, thin-grained Eastern barleys such as Ouchak.

Originally in the United Kingdom, malt for brewing was made from home grown barley only; of late years, however, very considerable quantities are imported from other countries as France, Germany, Denmark, California, Russia, Egypt, Algeria, Chili, and New Zealand; and Beaven also classifies these as follows:—

Chevalier Californian, Chevalier Chilian, Tripoli (Ouchak type), and Ouchak are the narrow-eared two-rowed type, *Hordeum distichum.* Brewing Californian, Mexican, Argentine, North African, Gaza, Smyrna, Black Sea, Danubian, Cyprus and Spanish are mostly of the four-rowed type, *Hordeum vulgare.* Brewing Chilian, Persian, and Beyrout are of the six-rowed type, *Hordeum hexastichum.* Mixtures of two-rowed and six-rowed barleys are, however, common in a good many foreign barleys.

Some of these barleys are much superior to the English in appearance, whilst others, although presenting anything but a favourable appearance, are nevertheless not to be despised, fulfilling, as they do, a useful purpose when judiciously mixed with our own. This we shall see later on.

The quality of barley, as one would naturally suppose, depends to a large extent on the nature of the soil, climate, manure, &c.

Cold clay land, which is stiff or tenacious, no matter how well drained it may be, can rarely grow really good malting barley (Stopes on Malt and Malting).

Barley requires a warm, friable soil such as the calcareous loams, &c., of Norfolk and the districts having a chalk subsoil, which are the best natural soils. Rich, loamy, or well-manured sandy, and other dry soils are also capable of producing fine barleys when the season favours them, especially if lime be present in fair quantities.

Barley flourishes best in the farmer's interest upon land well tilled and heavily manured, for it grows strongly and produces heavily. Such barley, however, is not the best for the brewer, for it has a higher percentage of certain nitrogenous matters which are decidedly injurious to the keeping properties of the finished beer. Hence the direct manuring of the soil for barley with nitrogenous manures (stable manure, salts of ammonia, and nitrates) must be avoided, such manures also produce a rank growth of the stalk and of the leaves; the barley is easily beaten down, and produces from this cause weak grains poor in starch.

Accordingly, Professor Farmer recommends that barley should follow wheat which in its turn followed roots. This seems to be reasonable, for it is now acknowledged that highly nitrogenous manures are decidedly prejudicial to the production of good malting barley. For malting purposes, the fine, full, well-developed bright grain is the best.

Climate exercises a more important influence on barley than soil or manure. Indirectly, a bad summer, and especially a bad harvest time, will almost invariably cause such defects in barley that the production of really good malt is impossible. The difference in price may not be very great, if viewed from the standpoint of first cost, but the deficiency of extract and the inferior quality of the wort produced add largely to the actual loss of the brewer.

For the production of sound light beers quick in brightening, it is imperative to secure a barley of high vegetative capacity. With our varying climate and high farming, English barleys are less suited for this purpose than those imported from other countries, and the superiority of foreign barleys over English is, no doubt, to be attributed to the more suitable condition of climate under which they have been grown and harvested.

10. **Characteristics of barley.** For malting purposes Stopes groups the qualities of barley as under *four essentials*: vitality, condition, maturity, odour; and *six desirable non-essentials*: size, weight, uniformity, colour, appearance of skin, age.

Upon the vitality of barley depends the growth, hence it is most important that the barley should contain as few non-germinating grains as possible. The most trustworthy test for this is that of enforced growth, and for this purpose Coldewe's apparatus (Fig. 2) is very effective.

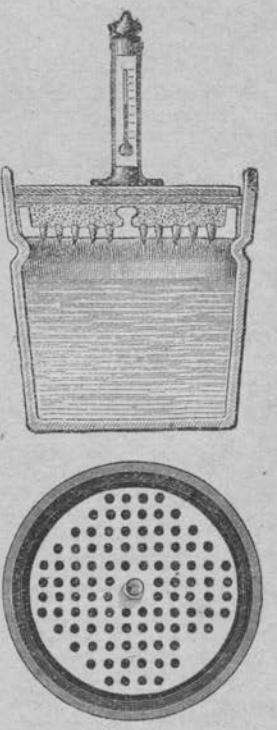


FIG. 2.

This consists of a receptacle for water, a germination tray, usually a porcelain plate provided with 100 perforations, and a felt cover fitted with a thermometer as shown in the figure. The corns to be tested are inserted in the perforations with the germ downwards, and a small quantity of moist sand placed round them. They receive the necessary moisture for germination with perfect equality from the receptacle underneath, whence the water evaporates without causing them to be exposed to an excess of moisture. The consequence is that corns of even quality not only grow as fast as they possibly can, but also perfectly alike, thus showing precisely the even or uneven germinating capacity of the grain, and as the tray is constructed to hold exactly 100 corns, the percentage is at once seen.

Other forms of apparatus in use for the same purpose are the 'Aubry' and 'Blaber,' which

consist of warm chambers or cupboards, in which the corns are germinated in a moist atmosphere. These appear to give better results than the Coldewe, and their capacity is greater, so that several barleys can be tested at the same time.

This test should show at the utmost only 4 p.c. of non-germinating grains. The above qualities may be briefly summed up:

The corns should not contain more than 4 p.c. of non-germinating grains.

When cut through, the cut surface should be white, friable, and mealy looking; if it is fatty, glassy, or spotted, it is not to be recommended for use.

Barley ought to smell fresh and clean, not musty or mouldy.

The corns should be as nearly as possible of one size, plump and heavy, and free from other seeds. A good heavy barley should weigh from 50 lbs. to 56 lbs. per bushel; all under 50 lbs. may be deemed light. The grains should have an even light-yellow colour, with a thin wrinkled skin.[1] Barley improves in vitality for the first few months after harvesting, and then declines, so that it is not safe to malt barleys more than two seasons old. The actual judging of particular samples with regard to quality and comparative value is a matter requiring great practical experience and skill, especially as often the bulk is bought from a mere cursory examination of the sample in market. Grain very hard to bite, can never be converted into good malt. It has been found that light passes readily through vitreous corns, but not through mealy ones, and this fact has been taken advantage of to distinguish between the two. The apparatus invented by Vogel is used for this purpose.

Barley should be neither over- nor under-ripe. Under-ripe corns have a bad colour, and feel cold to the hand. It is difficult to detect over-ripe grains. Mature dry grains slip through the fingers more readily than immature or damp ones.

One of the great difficulties of the present day, in addition to those resulting from bad harvesting and maturing of the grain, is the prevalence of damaged and broken corns. It is more difficult than ever to procure samples that are perfect in this respect, owing to the carelessness so prevalent during the threshing of the barley by modern methods, for we may have not only broken corns which are easily detected, but other corns, apparently sound and good, that show on closer inspection slight abrasions of the skin occasioned during threshing by the too close setting of the machinery. This is a source of much trouble to the maltster, giving rise to mould on floors as well as to a large proportion of non-germinating corns.

Attention has been drawn to the ill effects of this close dressing by several authorities, and quite recently Montagu Baird and C. H. Babington have been instrumental in inducing the Board of Agriculture to publish a circular drawing the farmer's attention to this matter, and recommending more careful methods of threshing.

11. **Structure of barley.** When a grain of barley is examined with the naked eye, a deep but narrow furrow may be observed running down the whole length of one side; the general appearance of this side is very convex, both laterally and longitudinally, hence it is known as the *ventral* side, and is the side which faces inwards when the grain is still attached to the ear. The outer or *dorsal* side of the grain is much flatter than the ventral. If next we cut through a grain of barley lengthwise with the furrow, so as to split it in two, three principal parts can be distinguished in it (Fig. 3):

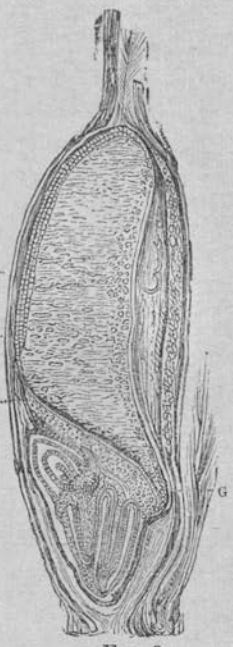


FIG. 3.

(1) The hull, or skin. (2) The endosperm, or starch substance. (3) The embryo, or germ.

The hull (F) or outer coat of the grain consists of the *paleæ* or valves, formed of three rows of differently formed cells. The hull can be easily peeled off the barley grain after steeping, and under this is a shell tightly enclosing the grain; this is the pericarp of the fruit, and beneath this and closely grown together with it lies the integument of the seed. The starch substance, or endosperm (E), forms by far the larger bulk of the barley grain.

The embryo, or germ, constitutes about $\frac{1}{7}$ of the corn, and lies on the lower end of the grain, and its point or apex inclines towards the smooth or unfurrowed side. The lobe of the seed proper in the shape of a flat shield, GG, the scutellum, forms the boundary between the endosperm and the embryo; which, lying as it does in close contact with the endosperm, serves as a special organ of absorption, through which, during germination, the nutritive matter stored in the endosperm must pass on its way to the growing portions of the embryo. A line of cells forming a well-marked *epithelium* separates the embryo from the endosperm. This also has the function of absorption of nutriment for the growing germ, but it is markedly differentiated from the other tissues by its specialised *secretory* functions.

Immediately below the scutellum and in intimate organic connection with it, are the main organs of the axis, the *plumule* and *radicle*. The former consists of four rudimentary leaves enclosed in the plumule sheaths, whilst the primary radicle with its root cap is completely imbedded in the root sheaths. The *endosperm* is principally filled with a mass of thin-walled cells, closely packed with starch granules, embedded in a very fine network of proteid material, and arranged with their larger dimensions parallel with the axis of the grain. The

[1] Faulty grains are frequently sulphured, but can be easily detected by an experienced person, on account of their unusually bright colour.

starch-containing cells are surrounded by a triple layer of thick-walled rectangular cells the so-called *aleurone cells*, the cell contents of which consist mainly of closely packed aleurone grains and fat, embedded in a protoplasmic matrix with well-defined nucleus. This layer does not, however, enter the embryo at any point, but is only in close contact with it.

Lying between the starch-containing portions of the endosperm and the embryo, is a comparatively thick layer of empty and compressed cells belonging to the endosperm. These cells are emptied of their contents during the later stage of the growth of the grain. The development of the embryo takes place at the expense of the endosperm, emptying its cells of their starch and protoplasm. The cell walls do not share the fate of the cell contents, but remain in the ripe grain, pressed tightly together by the growing embryo.

The changes which take place during germination are brought about by certain catalytic agents termed *enzymes*, and are threefold.

In the first place, there is the dissolution of the walls of the starch-containing cells by one of these enzymes, which action proceeds progressively from the proximal to the distal regions of the endosperm; in the second place, the dissolution of the starch granules thus set free, by a second enzyme, and the transference of the soluble products of the action to the growing points of the embryo; and finally, the breaking down of the complex nitrogenous or albuminoid bodies, which form the material of the endosperm cells, into simpler ones by a third enzyme, thereby rendering them available as food for the young plant.

12. **Chemical composition of barley.** Those substances which go to compose the barley grain, as well as the other cereals used in brewing, may be classified as follows:—

I. Carbohydrates. II. Resins and fats. III. Nitrogenous substances. IV. Ash.

The proportions of these several constituents vary with different kinds of barley, according to circumstances of growth, manuring, harvesting, climate, &c.

I. **The carbohydrates** contain the three elements, carbon, oxygen, hydrogen, and are so called because they may be supposed to be derived from the union of a certain number of molecules of water with an equivalent number of atoms of carbon.

The principal members of this group are (*a*) *cellulose, starch, dextrin*; (*b*) *maltose, cane sugar or sucrose, raffinose*; (*c*) *dextrose, levulose.*

As the chemistry of the carbohydrates is fully treated of elsewhere, there is no occasion to refer further to this subject here.

II. **Fats.** Only small quantities of fat are found in grain, and the amount contained in barley is about 2·5 p.c. It can be readily obtained from the ground corn by treatment with ether, which on evaporation leaves the fat as a thin yellow-coloured fluid of an agreeable odour, which is, however, soon replaced by an offensive one if the oil is allowed to remain in contact with air.

The composition of this fat has been investigated by many observers, and the following is its composition according to A. Stellwag:—

Fatty acids . . .	13·62 p.c.
Neutral fat . . .	77·78 „
Lecithin . . .	4·24 „
Cholesterol . . .	6·08 „

Resins. The outer coatings of most cereals develop in ripening a certain amount of resinous matter, which by its comparative insolubility protects the interior from premature access of water.

In addition to fat and resin, a number of other substances free from nitrogen and which are generally classed with the resins are also represented in the grain of barley. Very little is known of them, but although present in minute quantity they play an important part in contributing to the flavour and general appearance of each individual grain of corn.

III. **The nitrogenous or proteid bodies** found in grain are much more complex in chemical composition than the carbohydrates; they all contain carbon, oxygen, hydrogen, nitrogen, and some of them sulphur as well.

Several investigators have turned their attention to the nature of these bodies, and we are indebted to T. B. Osborne for much valuable information on this subject. This worker finds that barley contains the following proportions of proteid bodies:—

Leucosin (albumin) .	0·30 p.c.
Proteose, edestin (globulin) .	1·95 „
Hordeïn . . .	4·00 „
Insoluble proteid . . .	4·50 „
	10·75 „

Of these the *albumin* is soluble in water, but coagulated by heat, *globulin* is insoluble in water, but soluble in dilute saline solutions, *proteose* is soluble in water, and *hordeïn* only slightly so, but readily soluble in 70 p.c. alcohol.

In common with all other seeds and living vegetable as well as animal organisms, barley contains several of a remarkable series of bodies, which are considered to be closely allied to the albuminoid bodies, and which are termed *enzymes*. Up to the present no evidence has been brought forward to determine whether these bodies have a definite composition, for in spite of many investigations it has not been found possible to determine the constitution of a single one.

These bodies are termed unorganised ferments, and they effect fermentative processes. Effront defines them as active organic substances, secreted by cells which have the property under certain conditions of facilitating chemical reactions between certain bodies, without entering into the composition of the definite products which result. The ferments act specifically, that is to say, each one exercises its activity exclusively on substances of well-defined structural and stereo-chemical composition. Of the means by which these ferments develop their activity nothing is known. Their reactions must at present be simply regarded as special phenomena of the catalytic processes, catalytic reaction being a somewhat vague term which we apply to those reactions which cannot without further knowledge be explained by simple chemical theories. The *enzymes* have been divided into the following seven groups, according to their respective specific reactions

(W. J. Sykes, Principles and Practice of Brewing, 1907, 117):—

Group I.—Diastatic enzymes.

Diastase of secretion (malt) Translocation diastase (barley) Ptyalin (saliva)	Hydrolyse starch into maltose, glucose, and maltodextrins.
Glucase (maize)	Hydrolyses starch finally into glucose.

Group II.—Cyto-hydrolytic enzymes.

Cytase (malt) Enzymes of seeds in which the reserve material is cellulose	Transform cellulose into sugars such as mannose, xylose, &c.

Group III.—Pectin enzymes.

Enzymes which convert pectinous substances into vegetable jelly.

Group IV.—Inverting enzymes.

Invertase (yeast) Invertase (malt)	Convert cane sugar into invert sugar.
Maltase (yeast) Enzymes of the small intestine	Transform maltose into glucose.

Enzymes of yeast which degrade the dextrins to maltose; these are especially present in those yeasts which bring about the secondary fermentation and condition of beer.

Enzyme of kephir	Inverts milk sugar.
Probable enzyme of germinating barley	Converts maltose into cane sugar.

Group V.—Proteolytic enzymes.

Enzymes of malt and other vegetables, among which are peptase and tryptase Trypsin (pancreas)	Convert proteids into proteoses, peptones, and amides.
Pepsin (stomach)	Converts proteids into proteoses and peptones, but not into amides.

Peptonising ferments secreted by many bacteria.

Group VI.—Glucosidal enzymes.

Emulsin (bitter almond)	Splits up amygdalin into oil of bitter almonds, hydrocyanic acid, and water.

Many other enzymes which have the power of hydrolysing glucosides.

Group VII.—Zymase of yeast.

Splits up sugar into alcohol and carbon dioxide.

'Ferments,' as applied to these bodies, is hardly a very satisfactory name, and it has been suggested, and the suggestion has been adopted to a large extent, that those enzymes that bring about the hydrolysis of substances should be termed *hydrolysts*, and by combining the word 'hydrolyst' with the name of the susbtance acted upon, we get a distinctive name for each class. Thus an enzyme capable of inducing the hydrolysis of starch is termed an *amylo-hydrolyst*; one which affects proteids, a *proteo-hydrolyst*, &c.

Rôle of enzymes during germination.—As already mentioned, the embryo of the barley corn is in close contact with the starchy part of the grain, the endosperm, which is the storehouse of all the nutriment required by the young plant until such time as it can lead an independent existence and acquire necessary food from the air and soil. The enzymes during this period convert the insoluble starch and nitrogenous matter into soluble bodies, which can easily travel to the growing germ.

Ungerminated barley contains an enzyme or amylo-hydrolyst, usually known as translocation diastase, which differs from the amylo-hydrolyst or diastase, which is present in germinated grain, in its inability to liquefy starch paste; the latter having extremely active liquefying and saccharifying powers.

If a cold-water extract of barley be added to starch paste, it is found to have no action whatever. If, however, this starch paste be first treated with cold-water malt extract, at a temperature of about 75°C. for a few minutes, so as to bring it into the form of soluble starch or *erythro-dextrin*, then cooled to a temperature of 50°C., and some cold-water barley extract added, the conversion of the soluble starch or higher dextrins into reducible sugars proceeds with great facility.

Translocation diastase is unable to corrode starch granules, Brown and Morris stating that this power and that of liquefying gelatinised starch appear to go hand in hand.

Lintner and Eckhardt found that the action of barley and malt diastases differed considerably at various temperatures (Zeitsch. für Brauw. 1889), and J. L. Baker has shown (J. Chem. Soc. 1902) that the products of reaction on a solution of soluble starch by barley diastase are very different from those of malt diastase.

As soon as the barley corn begins to germinate, the more active amylo-hydrolyst, termed by Brown and Morris *secretion diastase*, to distinguish it from the diastase already present in the grain, makes its appearance, and according to these authors, is principally due to a secretion by the columnar epithelium of the growing embryo. There is a steady accumulation of this diastase in the endosperm, which in the course of time permeates its whole tissue, the ready passage of the enzyme through the contents of the grain having been enormously facilitated by the previous destruction of the cell walls by the cyto-hydrolyst.

When this is accomplished, the malt acquires the so-called mealy condition which the maltster endeavours to bring about to its fullest extent.

Secretion diastase was first investigated by Payen and Persoz, in 1883, who gave it the name diastase from διάστασις (separation), on account of its supposed property of separating the interior of the starch granules from their outer envelope. Under the action of this diastase, starch which has been first gelatinised by boiling water undergoes a series of hydrations and successive decompositions, resulting in the production of maltose and dextrin. The action, which is capable of taking place at 0°C., attains it maximum between 60° and 65°C., and ceases altogether at 80°C.

It appears, then, that malt contains at least two *amylo-hydrolysts* or *diastases*, one of which, formed during the *growth* of the barley, has not

the power of transforming a saccharifying starch paste until it has been first converted into soluble starch; the other, formed during *germination* on the malting floors, possesses the power to a very marked degree of saccharifying starch paste even at as high a temperature as 80°C.

Brown and Heron (Chem. Soc. Trans. 1879, 596) formed an opinion that these bodies were not simple chemical compounds of constant definite composition, but must be considered as a mixture of several bodies differing from each other in chemical and physical properties. They ascertained that when cold-water extracts of barley and malt are heated up to different temperatures, for each increase of temperature there is a distinct and definite amount of coagulation of soluble albuminous substances, and at the same time a diminution in the diastatic energy of the solution, from which they conclude 'that the diastatic power of malt is a function of the coagulable albuminoids themselves, and is not due to the presence of a distinctive transforming agent.' There can be no doubt that during the kilndrying of malt a similar reaction takes place, especially in the earlier stages of drying; a small proportion of the more easily coagulable albuminoids being rendered insoluble, the diastatic power, which had attained its maximum at the withering stage, at the same time being diminished to a considerable extent. Indeed, it is a well-established fact, that a high-dried malt will produce in the brewing a more highly dextrinous beer than one which has not been dried at so high a temperature on the kiln. Another set of enzymes which are secreted during germination are those that act upon the proteids, the proteo-hydrolysts. It was not until quite recently that the presence of these enzymes were definitely decided in the affirmative, although it has long been known that the nitrogenous bodies of barley undergo considerable modifications during germination, and Weiss (Zeitsch. f. physiol. Chem. 31, 78–79; and Zeitsch. ges. Brauw. 1903, 19, 301) has proved fairly conclusively that the two enzymes, peptase and tryptase, are present. *Peptase* degrades the proteids down to albumoses, having a maximum activity at 51°C., and *tryptase* degrades the albumins down to amides, &c., the optimum temperature lying between 45°C. and 50°C. The action of both enzymes ceases at 70°C.

The embryo of the barley corn during development requires nitrogen to build up new protoplasm, in addition to the carbohydrates supplied to it with the help of the diastase, and the mineral salts. There is therefore a continuous draft on the nitrogenous as well as the carbohydrate reserves of the endosperm. These nitrogenous reserves reside for the most part in the fine network of the material in which the solid starch grains are embedded, and consist of a complex mixture of proteids with very different properties. Some are soluble in water (15–16 p.c. of the whole), whilst others require reagents to bring them into solution. These proteids require previous preparation before they can be absorbed by the embryo.

This preparation is brought about by the enzymes above described, the peptase reducing the proteids to albumoses, and the tryptase further reducing the albumoses to the amino-acids, &c., and it is mainly in this form that the nitrogen wanders through the scutellum into the young plant.

Brown estimates that about 35–40 p.c. of the nitrogenous reserves of the endosperm pass into the young plant, and it is probable during the ordinary malting period that at least 60–70 p.c. of the proteids have been altered, while only 16–17 p.c. of the reserve starch has been attacked in the same time.

The nitrogenous bodies found in malt are due to two quite different but complementary processes going on simultaneously, viz. the breaking down of these substances into less complex bodies, which goes on in the endosperm, and the building up of these simpler bodies into new complexes, which goes on in the growing embryo—a down-grade and an up-grade process. About one-half of the nitrogenous bodies of malt are up-grade products of the processes of germination. This appears to be the explanation of the fact that the conditions which tend to force the growth of the vegetative parts of the grain are just those which tend to increase the proportion of the permanently soluble nitrogenous constituents of a malt.

H. T. Brown (The Nitrogen Question in Brewing, J. Inst. Brewing, 1907, 5) has investigated the nature of the nitrogenous bodies soluble in water and not coagulated on boiling, present in the finished malt, and was able to determine about 66 p.c. of the total.

Taking the nitrogen of a previously boiled extract of malt as 100, he found its distribution amongst the various classes of constituents came out approximately as follows:—

Ammonia nitrogen	3·5
Malt albumose nitrogen	20·0
Malt peptone nitrogen	31·0
Amide and amino nitrogen	8·5
Nitrogen due to organic bases	4·0
Balance of N still unaccounted for	33·0
	100·0

This gives a synopsis of the various classes into which they are divided. It was found that the albumoses consist of at least three distinct bodies, albumoses I., II., and III.; whilst the peptones can be differentiated into two malt peptones, I. and II. The 8·5 p.c. of nitrogen attributed to amides and amino-acids includes *asparagine*, *tyrosin*, and *leucine*, and *allantoin* is also included. The 4 p.c. of nitrogen corresponding to organic bases mainly represents *betaine* and *choline*.

The following table, deduced by R. Warington from a compilation of all accessible analyses, numbering 56 in all, may be taken as showing a fair average composition of barley grain:—

1. Carbohydrates	63·66
2. Fibre	7·09
3. Fat	2·05
4. Albuminoids	10·58
5. Ash	2·57
6. Water	14·05
Total	100·00

Barley grain contains on an average less nitrogen than either wheat or oats; the proportion is least in fine malting barley, amounting to only 8 or 9 p.c. of albuminoids.

IV. The **ash** of barley grain, as calculated

from 50 analyses by E. Wolff, has the following average composition :—

Potash . . .	K_2O	21·35
Soda . . .	Na_2O	2·25
Lime . . .	CaO	2·74
Magnesia . .	MgO	8·66
Ferric oxide . .	Fe_2O_3	0·91
		35·91
Phosphoric anhydride	P_2O_5	35·19
Sulphuric anhydride .	SO_3	1·72
Silica . . .	SiO_2	26·10
Chlorine . . .	Cl	0·88
		63·89

The bulk of these phosphoric acid compounds in barley ash exist as a calcium-magnesium-potassium salt of oxymethylenediphosphoric acid, while about 5 p.c. are present as lecithin-phosphoric acid.

It has already been stated that land which has been highly manured with mineral salts containing a high percentage of nitrogen, such, for instance, as sodium nitrate or ammonium sulphate, will produce a heavy crop of barley. This, of course, from a farmer's point of view, is decidely an advantage, but such barley is always found to be exceedingly rich in albuminoids, and consequently low in the percentage of starch. Hence for brewing purposes it is extremely unadvisable to use such a barley, for not only will the wort resulting from the malt made from this barley be poor in saccharine matter, but these nitrogenous substances, when present in too large proportions in the wort, exercise a very injurious influence on it, and cause the finished beer to become thick and cloudy and prevent its keeping sound for any length of time (L. Marx, Rev. Univ. de la Brasserie).

Therefore, from a brewing point of view, a barley rich in albuminoids must be regarded as of poor quality, while a low content of albuminoids in general is an expression of high quality. Hence Maercker (Bied. Zentr. 1885, 696) concludes that the weight per bushel which is generally regarded as a fair criterion of the value of a barley, can hardly be looked upon *alone* as a safe guide with regard to quality, but that the chief characteristics of a first quality barley are (1) its consistency; (2) its colour; (3) percentage of moisture; and (4) its percentage of albuminoids; these in first-class barleys should not exceed 8·6 p.c. He also finds that a grain possessing a fine, thin husk is found to yield the largest amount of starch; the kernels in this case should be thin and rounded, the percentage of husk being a minimum. This is the view adopted by Prof. Brewer, of the Brewer's Experimental Station, New York, as well as by C. Lintner, Dingl. poly. J. 247, 350), who gives 10·5 p.c. of albuminoids as a limit for first-class barley.

13. Preparation of barley for malting. Very little barley is in a fit condition for undergoing the process of malting when it is delivered at the brewery or malthouse by the farmer, as it generally contains several varieties of foreign seeds, fragments of pebbles, &c., mixed up with it, as well as light and damaged corn. The following preparatory stages are considered by Stopes to be generally needed :—

Cleaning, grading, kilndrying or sweating. The dust which is generally found adhering to barley consists to a large extent of spores of numerous ferments and fungoid organisms, many of which find their way into the fermenting round; seeds of weeds and other foreign grains may also be present.

C. G. Matthews (J. R. Microsc. S. 1883) found that various kinds of barley, English as well as Saale, French, Chilian, and Californian, yield, when steeped for a short time in water, an abundance of mould spores, bacteria, and infusoria of various species, and from many experiments made by him he concludes that in the first stage of malting, when the barley is put in steep the spores of various moulds and other micro-organisms are present in quantity in the steep water, being introduced into the cistern with the barley, and although the greater portion may be removed on withdrawal of the steep water, yet there would in all probability be left sufficient to cause a mould growth, on injured or weakly corns whilst on the malting floor. Now, it is a well-known fact that good, healthy, growing, perfect corns are never found to develop growths of any kind of mould; the corns which appear to be favourable to such are always those which from various causes are incapable of carrying on a strong and healthy growth, having been injured by heating in stack, or sprouting, or, as is more generally the case nowadays, been split, crushed, or otherwise damaged during threshing, a slight abrasion of the skin in some instances being sufficient to give rise to development of mould. Hence it will be seen how very important it is that the barley should be cleaned and freed as much as possible from dust, broken corns, and all other matters which may in any way encourage the growth of mould on the malting floors, so that if a maltster wishes for clean floors he must first thoroughly clean his barley of such objectionable bodies by proper and careful screening. A form of screen which

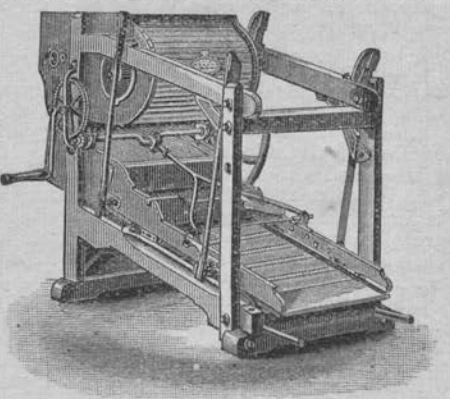


FIG. 4.—SELF-ACTING MALT-SCREEN.

seems well adapted for this purpose is shown in Fig. 4.

Grading grain is, if possible, still more important than cleaning it, as it is most desirable that for malting purposes all the corns should as far as possible be of uniform size. The next process, and one of extreme importance, is the

kilndrying of barley, or sweating, as it is technically termed. With cold and damp seasons, and with the modern fashion of threshing by steam either when carting or almost immediately after stacking, so that the grain has had no chance of sweating in stack, it is highly desirable that this should be done on the kiln, but, like every other operation in malting, it requires discrimination and the exercise of judgment. Broadly speaking, almost every sample that has not been influenced by damp is decidedly the better for a few hours upon the kiln prior to storing or steeping. If the acrospire has moved, then drying does more harm than good.

The moisture percentage should be determined on each parcel, and those parcels which contain a larger percentage than 12 should be dried (or sweated) to expel any excess over this figure.

Great improvement in germinating power is brought about by this sweating, which is ascribed to the following causes: (1) the removal of dirt from the skin of the corn and consequent freeing of the pores; (2) the removal of moisture from the endosperm cells causes them to draw together slightly and so gives rise to pores and passages through which the steep water may reach the centre of the grain,—excess of original moisture causes these cells to swell and become tightly pressed together; (3) the expulsion of moisture considerably increases the secretory function of the embryo as regards the amylo-hydrolytic and cyto-hydrolytic enzymes.

Sweating is best carried on at a low uniform temperature, rarely exceeding 105°F. Schönfield states that excellent results are obtained by gradually raising the temperature of the barley to 133°F., and maintaining this temperature with a liberal supply of air until sufficiently dry. When dried it is advisable to store the barley in bins for at least a fortnight prior to steeping, in order that it may have time to mellow. The grain is now in a suitable condition for undergoing the various processes of malting; these are steeping, couching, flooring, withering, drying.

14. The chief distinctive difference between malt and corn is growth; no matter what processes they may have been subjected to, any grains of the corn which have not grown remain as barley, wheat, &c., and are not malt. When a seed is placed under suitable conditions with regard to heat, light, air, and moisture, it begins to germinate or grow. When it begins to grow the first sign of a change taking place is the protrusion in a downward direction of the rootlets or radicle through the integument; at the same time, the plumule or acrospire begins to start growing in an upward direction until it bursts through the integument and gives rise to the first leafy organs of the growing plant. When wheat commences to germinate, the plumule of the embryo on bursting through its envelope finds itself in immediate contact with the inner surface of the pericarp, which in this case not being sufficiently strong is ruptured, the plumule continuing its growth outside the grain.

In barley the pericarp is of sufficient strength (even in the so-called naked barley, where the palea, as in wheat, is not adherent) to retain the plumule within it. In consequence of this the growth of the plumule takes place between the testa and pericarp, and in very close proximity to the reserve materials of the endosperm, until it finally issues at the end of the grain the farthest removed from the embryo.

15. The water used for wetting or steeping should be of such purity that it may pass as drinking water. Waters containing much organic matter, especially that derived from animal sewage, frequently contain salts of phosphorus, which, coming in contact with the numerous spores of bacteria and mould on the surface of the barley, afford a most favourable medium for their development and growth. Certainly the water in which barley has been steeped affords itself very suitable nourishment for these micro-organisms, and where the water helps in the same direction the result is self-evident.

Of the mineral matter in water iron in any form is most objectionable, as it gives rise not only to the insoluble phosphate of iron, but it also forms with the tannin in the husks of the grain, the black insoluble tannate of iron which remains in the husk and discolours the grain.

Chlorides of the alkalis, if present in large quantity, remove a considerable proportion of mineral as well as organic matter, whilst they retard germination to a considerable degree (Michel and Handwerck, Bied. Zentr. 1882, 486).

The presence of calcium chloride hinders the extractive action of sodium chloride to a certain extent (*ibid.*).

Hitherto it has been generally accepted that when barley is steeped in the cistern, the steep water extracts matter not only from the husks, but also from the interior of the grain; and differing views have been advanced regarding the influence which hard and soft waters exert on the extraction of organic matter and phosphates from the interior of the grain. Ullick found that calcium and magnesium carbonates and sulphates are generally supposed to fix the phosphoric acid in the grain, the potash and magnesia being extracted by the hard water, whilst the lime enters into combination with the phosphoric acid, forming an insoluble phosphate in the grain (Ullick, Bied. Zentr. 1882, 40–42); but Mills and Pettigrew found that the more of these mineral salts there are in steep water the more mineral matter there is extracted from the barley (Chem. Soc. Trans. 1882, 38). They were confirmed in their results by Michel and Handwerck (Dingl. poly. J. 247, 82, 168, and 214). From a series of experiments made by the author on the steeping of barley, where (1) distilled water alone, (2) a water containing 13·8 grains of calcium carbonate per gallon (*v.* Analysis No. 2, p. 352), and (3) the same with 30 grains of gypsum added, were employed, the following results were arrived at: that the total matter extracted by water No. 1 was in all cases the greatest, that by water No. 3 least; that this applied to the mineral as well as the organic matter, but whereas No. 1 dissolved out the most mineral matter, No. 3 extracted the most phosphoric acid.

Mills and Pettigrew conclude that nitrates have a highly stimulating action on the germination of malt, and recommend the addition of a small quantity of calcium nitrate (about 3 grains per gallon) to those waters which are deficient in nitrates.

A. J. Brown, however, has proved (J. Inst. Brewing, 1907, 13, 658) that when undamaged barley corns are steeped in either hard or soft waters the salts dissolved only penetrate the outer thick coverings of the grain, and the first thin skin, or *pericarp*, but are arrested by the second thin skin, or *testa*, which immediately surrounds the germ and endosperm, only pure water entering the grain. Hence the action of steep water is limited to the external envelopes of the grain, and the matter extracted during steeping (varying from 0·5 to 1·5 p.c.) must be considered to be derived in its entirety from the skins of the barley corn. Working on these lines, H. Seyffert (Zeitsch. ges. Brauw. 1907, 30) finds that the carbonates of the alkali earths (sodium, magnesium, and calcium) act on the tannin and bitter principles of the husks (the effect being to remove them or render them harmless), giving the malt an aroma and greater sweetness. This author considers very soft waters unsuitable for steeping, and only give good results with very fine thin-skinned barleys, for the greater the carbonate content of the water, the less stress need be placed on the quality of the barley. Moufang and L. Vetter confirm the views of Seyffert, and also add that calcium sulphate and sulphuric acid in steep water cause the husk constituents to adhere more firmly to the fibre of the husk, so that these substances can only be removed by subsequent treatment with alkaline water. Matter in solution in the steep water, however, enters damaged corns, and loss of extract from the interior of the grain takes place in any type of water, which fact strengthens the objection to the damages of close threshing.

It will be seen, then, that, contrary to previous views, the most favourable water for steeping is one containing alkaline carbonates.

The temperature of the steep water considerably effects the rate at which the grain absorbs water, and also the speed of germination on the floors. The warmer the water, the more rapid is the absorption, and the quicker the start of germination. The temperature usually adopted in England is 50°–55°F., and care should be taken to see that this is kept constant, in order to preserve regularity of water content and growth.

The use of lime water in the steep has been recommended by Windisch to improve germination and to avoid mould formation on the floors. This has been found to give good results, the lime water being used in the first change only.

16. **Malting.** At present three systems of making malt are practised:

(1) English system.
(2) Continental.
(3) Pneumatic.

The English system briefly consists in steeping the grain in water in large iron or stone cisterns, draining the water off, spreading the moistened grain in thin layers upon exposed floors and drying upon an open fire kiln at a period of from 9 to 21 days from time of steeping.

The continental system differs materially in all the above details.

Pneumatic malting provides for absolute control over the admission of air supplied to the germinating grain.

Briefly the system is as follows: The grain is first steeped in the same manner as in the English floor system. It is then transferred to the interior of a metal cylinder or drum, which is rotated slowly in order to keep the growing barley on the move, whilst moist air is blown through the grain from a central duct; by this means absolute control of temperature and humidity is obtained, and the necessity for sprinkling is obviated; when the piece (as the drum load of growing barley is termed) has grown to the desired extent it is either transferred to an ordinary kiln or dried in the same drum, hot air being blown through instead of cool moist air until the piece is sufficiently cured.

The simplest form of malthouse possessing any capacity for work is a plain two-story building having attached to it a kiln or drying-house, and consisting of a ground-floor of clunch, a brick steeping cistern, and a first floor of timber with or without partitions for separating the stored grain or malt; but a good malthouse of fair size is most conveniently and favourably worked if it consists of one main building of three stories—two kilns and a corn or malt store.

The growing floor may be composed of a variety of materials, but that which is most to be preferred is either cement concrete worked to a perfectly smooth face, or plain unglazed red tiles, well set in cement.

The cistern should always be at the end opposite to the kiln in a single-floor house, and so arranged that entire control of the temperature of the steep liquor can be secured, and that the grain can be readily screened into them when filled with water to enable the thin corn and refuse to float off.

The water supply should be so arranged that it can be run in from below and overflow at top prior to a charge of steep liquor, and a number of inlet and outlet pipes, all fitted with strainers, should be fixed. There should be in addition a series of perforated pipes, by means of which water can be sprayed or sparged from above over the grain like a shower. The cisterns are emptied of the steeped grain either by shovelling on to the floor, if on the same level, or by running down through shoots in the bottom to the floor below.

Cisterns are generally built of concrete, brick, or iron. An excellent form of construction is afforded by the use of the Hygeian Rock cement, as shown in Fig. 5. This method gives a wall only 9 inches thick, but quite strong enough for all practical purposes; the outside wall of the cistern is generally coated with cement, whilst the interior of the cistern is preferably lined with white glazed or enamelled bricks well set in cement. Brick or concrete cisterns should have a wide central channel running their full length. The top of the channel must be framed to receive perforated iron plates or tiles to serve as strainers. Iron cisterns are best made square in shape, with a conical bottom with a valve at the apex to discharge the wet

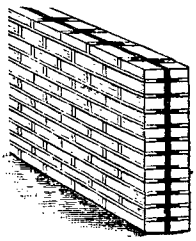


FIG. 5.

grain, the draw-off cock for the steep water being fixed as close to the valve as possible, and being covered with a perforated plate to prevent the barley corns being drawn off with the water. Such cisterns are usually fixed above the growing floor, and the grain is discharged directly on to it. The capacity of these cisterns should be ample enough to steep the utmost quantity of corn the floor can possibly grow in the coldest weather; not less than 14 cubic feet per quarter should be allowed when calculating their dimensions.

The kiln should be a lofty and roomy structure, preferably of brick, with a high roof surmounted by a cowl. The area of the drying floors should never exceed one-fourth or be less than one-sixth of the growing floors, nor should the combined air inlets and discharges bear a ratio to each other exceeding that of 4 to 5.

In practice it is found that the more closely a kiln resembles a chimney in construction, the greater is its effective capacity, consequently the tendency has been constantly to increase the height of the kilns. Kilns may be of various forms, but a square one is undoubtedly the best. In Fig. 6 is shown a type of kiln at one time very common in Great Britain.

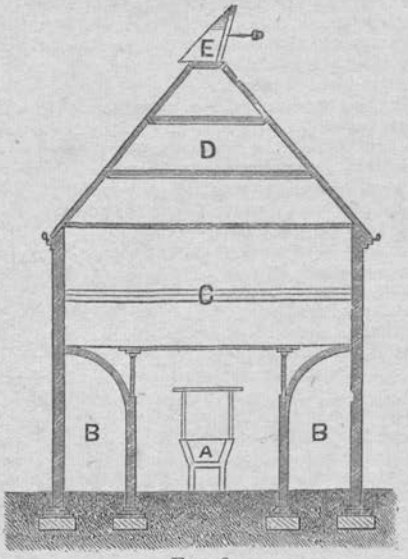


FIG. 6.

In every portion of the plant connected with malting, great diversities of size and style occur, and kiln furnaces offer no exception to the rule. Generally malt-kiln furnaces either permit the products of combustion to pass through the malt whilst drying, or they do not do so. The form of furnace, perhaps, most in vogue in this type of kiln is known as the fire-basket. This is a large open cast-iron basket of from 3 to 6 ft. square, with legs or supports carrying a frame fitted with ordinary fire-bars and thick sloping sides. These baskets are sometimes placed merely upon the bottom floor of the kiln with no protection of any kind, others are built over with a brick arch left full of holes for the escape of heat on all sides. A in Fig. 6 shows the form of fire-basket usually employed, the spaces BB at the sides of the furnace are used as coal or fuel stores. The drying floor C is built at all heights, ranging from 5 to 29 ft. above the furnace, and is generally made of earthenware

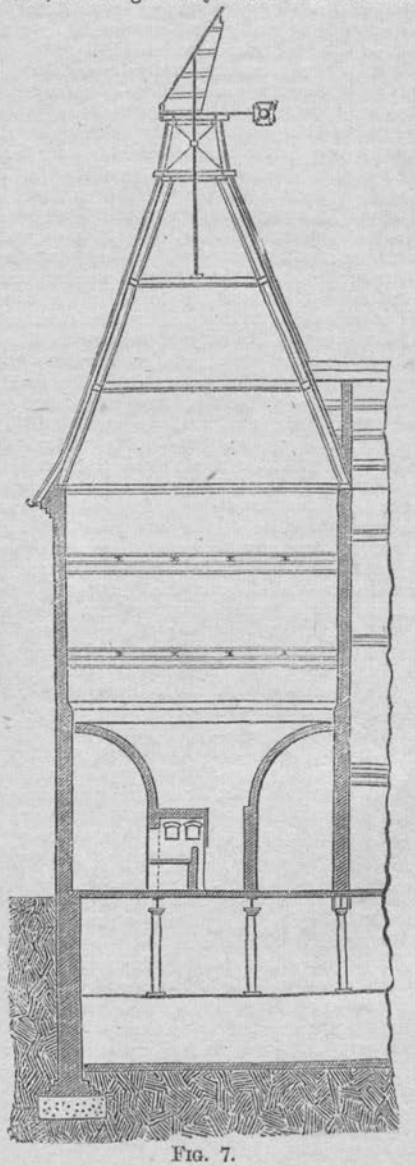


FIG. 7.

perforated tiles resting on light iron bars, which in their turn are supported by larger joists.

The construction of the roof D is of great importance, as very much depends on it; if the pitch is not at the proper angle, the drying of the malt is affected to a certain extent; cross timbers are objectionable, and should be avoided as far as possible; lath and plaster forms the best lining to the slate roof, as well as for the sides of the drying chamber.

The cowl E is the usual form of outlet to

this type of kiln. In 1881 the first kiln in England with two floors, and known as Stopes's system (Fig. 7), was erected by Messrs. Taplin & Sons, at Brighton, which gave very satisfactory results, and is used by many breweries in this country. It is claimed that two-floor kilns possess several advantages, of which, probably, the chief are the regularity of temperature upon both floors and the economy of fuel and labour.

The modern type of kiln is illustrated in Fig. 8. With this type the furnace A consists of a square chamber lined with fire-brick, and furnished with ordinary fire-bars. The temperature of the upward draught is regulated by iron plates which control the air inlets

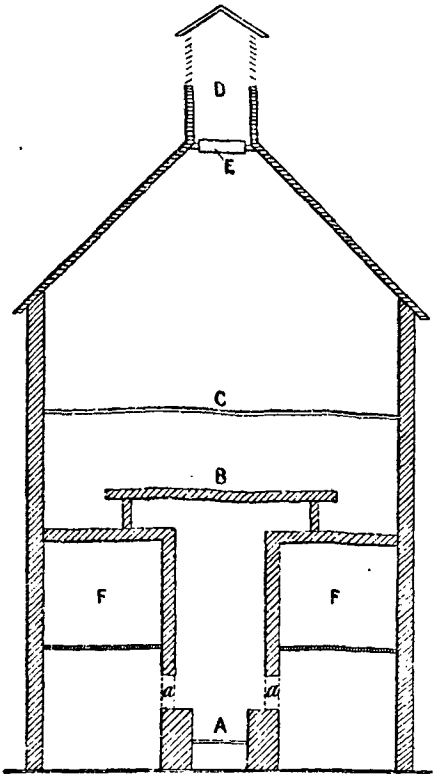


FIG. 8.

aa above the fire. The hot air and products of combustion pass up the shaft, and are distributed evenly over the drying floor C by the brick and concrete baffle B, supported on short brick pillars. The drying floor C is composed of steel wire. The cowl is replaced by a shaft D, provided with louvre boards, and a fan E to control the force of the upward draught is fixed at the base of this shaft. The spaces FF are used as a malt stores.

17. **Steeping.** The cistern should be filled with the steep water, then the barley slowly run through a shoot into the cistern; by this means the dirt and dust, small and light corns, and other matters find their way readily to the surface and may be skimmed off. This first steep water should be run off within the first six hours, it being the most impure; the succeeding steep water should be changed every twelve to twenty-four hours, according to temperature and season of year.

Sufficient time must be allowed between running off the old and running on the fresh water to allow the barley to become well aërated. In some maltings air is pumped into the barley whilst it is steeping in the water.

The first steep water should be run off from above, and the second water run in from underneath; this upward filtration serves very effectually to cleanse the grain from any adhering impurities. Some maltsters sparge on the steep water through sparge arms fixed above the cistern, thereby aiding aëration considerably. The grain is allowed to remain in steep for a period of forty to seventy hours, depending upon surroundings; but the maltster would naturally be guided by the temperature of the atmosphere, the quality, condition, and age of the barley, high temperature necessitating more frequent changes of steep water and shorter time in steep. Then, again, coarse, thick-skinned, or heavy barleys would naturally require longer steeping than the lighter and thinner kinds; the older the barley, the longer it requires to be steeped, as new barley germinates more quickly than old, the chief object of steeping being to impart to the grain about to be malted a sufficiency of moisture to ensure perfect and regular germination.

18. **Couching.** Before the repeal of the malt tax the barley, when taken out of steep, was placed in what was known as the couch. This might be regarded as a dry cistern where the grain had to lie a certain number of hours, or until it was gauged by the excise officer and the duty levied. Since this has been done away with, the couch is no longer needed, though even yet many maltsters pile up the barley when taken out of steep in a heap for twenty to twenty-four hours, indeed, until the growing point of the rootlet begins to show. This is a great mistake. In the first place, a greater amount of heat will be developed in the interior of the heap than on the outside by the germinating grain, hence these corns will grow more rapidly than the others, so that very uneven 'pieces' on the floors will be the result. It has also been proved that heat in couch tends directly to produce acidity in the finished malt. After the grain comes out of steep it requires all the oxygen it can get, as well as the removal of the carbonic acid gas which becomes disengaged by the process of germination; this necessarily involves free contact with air, and therefore it is advisable that couching be done away with altogether.

19. **Flooring.** Where it is still practised, as soon as germination is observed to have commenced, the couch is broken down and the grain spread out on the floor, the depth at first varying from 12 inches to about 3 or 4 according to season and temperature; it is then left for from twenty to twenty-four hours, when it is turned by means of a wooden spade. For the succeeding two or three days it is either 'ploughed' or turned about twice daily; of course this entirely depends on the judgment and experience of the maltster, his main object being to obtain a good bushy root and a regular

development of the acrospire. This requires very careful and close attention on the part of the maltster, for during 'flooring' he has not only to control the development or growth of the germinating grain, but the very nature of that growth. He has to give air and secure ventilation, to regulate heat and humidity, to foster the development of the acrospire, and check the root growth, or *vice versâ* as the case may be; all this can only be attained by long experience ,and an intelligent appreciation of scientific facts.

As a rule, English maltsters allow germination to proceed until the acrospire has extended to about three-fourths the length of the grain, the rootlets being at the same time about twice the length of the grain, but this is varied considerably according to the ideas of each individual maltster. Germination is accordingly carried on until this stage is reached.

About the fifth day from the time of taking out of steep the grain is sprinkled at intervals with water from a watering-can; this is continued until the sixth day. The quantity of water used for this purpose varies from three to six gallons per quarter of barley, but of course will naturally depend upon the state of the atmosphere as well as on the condition of the piece. On the days of sprinkling the grain is turned four times each day; after the sixth day it is turned two or three times daily. As soon as the germination has proceeded to such a degree as may be desirable, it is subjected to the process of withering, the object being to arrest germination, to increase the temperature of the piece so that as large an amount of moisture as possible may be got rid of preparatory to kilndrying. In many malthouses a proper withering floor is provided, generally of wood. During this stage the rootlets wither, becoming shrivelled and dry. As soon as this takes place, many maltsters throw the green malt, as it is now called, into a heap, and allow it to heat spontaneously, the object being to make it tender.

A piece which was sprinkled on the fifth and sixth days under ordinary conditions should be ready to go on kiln on the tenth or eleventh day.

Some maltsters allow the piece to become almost dry, not sprinkling until the eighth or even ninth day, but this cannot be recommended. The grain at time of going to kiln is at most only imperfectly withered, contains an excess of moisture necessitating very frequent turning as well as encouraging the growth of mould on kiln, and finally imparting a degree of hardness or steeliness to the finished malt which occasions diminished extract and possibly starchy worts.

If the barley whilst on the floors shows much, or in fact any signs of mouldiness, both the cistern and floors must be thoroughly well scrubbed with water to which 10 p.c. of good strong calcium bisulphite has been added. When dealing with low-class, ill-conditioned, or damaged grain, it is always well to add a suitable quantity of bisulphite, both to the steep water as well as to the water used for sprinkling.

It is also essential that thermometers should be placed at frequent intervals on the floors, and the temperature carefully noted from time to time; indeed, the question of temperature is just as important a factor in malting as it is in mashing.

20. **Drying.** By the time the germinated barley is ready to go on the kiln, it really is in effect no longer barley but malt, or more properly green malt, and has attained at this stage its highest diastatic energy, so that if the object were merely the production of diastase the malt might now be dried off at ordinary temperatures; but for the purposes of the brewer and distiller it is absolutely necessary that this green malt be subjected to the influence of heat, not only for the purpose of drying it completely and arresting germination, but in order that certain changes may take place in the chemical composition of its various constituents which are necessary to impart flavour and other properties to the liquor brewed from it and which we term beer. In addition to this, the malt also becomes capable of lengthened storage, and when well dried is best adapted for grinding and for transport; also all mould and fungoid growths are completely arrested and their vitality suspended.

The temperature employed in finishing off the malt on the kiln will determine its quality, thus we may have pale malts, medium, and high-dried.

For pale malt only the better qualities of barley should be used, and great attention should be paid whilst on the growing floor to prevent the development of mould; also the withering off should be carefully attended to, the principal object of the maltster being to obtain a good healthy growth in the earlier stages, and that the green malt should be as dry as possible at the time of going to kiln.

To dry pale malt well, Stopes says three things are necessary:

(1) It should be loaded in the condition just described as sound green malt upon a floor at a thickness rarely, if ever, exceeding 7 to 8 inches.

(2) It must remain *unturned* at a low temperature until nearly all moisture is removed.

(3) Heat must then be applied steadily and freely, and be maintained for a considerable time at a nearly uniform temperature, ranging from 160° to as high as 230° in some cases.

Constant forking of the kiln at this period is necessary, otherwise mould is specially liable to take place, and this should be persevered in until the malt is sufficiently dry to be turned. On no account should turning be resorted to until the malt is fairly dry to the touch. To ensure the carrying out of these points with greater accuracy and less risk than is possible on an ordinary kiln, the employment of a fan is requisite to create a motion of air through the malt, by which means the moisture can be extracted at much lower temperatures than would be possible under ordinary circumstances, and without fear of putrefaction, whilst for uniformity of temperature it is unequalled.

As long as an appreciable amount of moisture remains in the malt, it is most important that the temperature on kiln should not exceed 120°, while special attention must be paid to ventilation. When we consider that from 90° to 120° is the most favourable range of temperature for the development of the numerous

spores of various micro-organisms which, despite all our efforts to the contrary, are to be found adhering to the moist corns, and that with their development ensue chemical changes, such as the production of various organic acids, which most seriously affect the character of the malt, it would seem that the shorter time the malt is exposed to this temperature the better; therefore it is advisable that the layer of malt should certainly not exceed 8 inches, and it would be better still if it were only 6. But it is not simply a question of drying the malt quickly at a low temperature; certain changes irrespective of those produced by micro-organisms are brought about in the nitrogenous as well as in the other constituents of the malt whilst submitted to these conditions of temperature and moisture.

As soon as the malt begins to present a dry appearance, the temperature may be gradually raised up to the final temperature at which it is to be finished off. It is impossible to give a fixed limit for this, as a great deal will depend upon circumstances, but, as a general rule, for pale malt the final temperature may be taken at 200°F. From the time of raising the temperature until the end of the process, the malt should be turned at intervals.

In drying the malt the great point to be observed is the maintenance of a perfectly even temperature, so that the whole of the malt drying should be at any given moment of the same uniform temperature.

In the old type of kiln the process of drying, from time of going on to coming off kiln, usually occupies about four days, and is distributed as follows:

1st	day	not below	80°	or above	100°F.
2nd	,,	,,	90°	,,	110°
3rd	,,	,,	120°	,,	130°
4th	,,	,,	140°	,,	180°–185°

For the first two days the malt should on no account be turned, but the surface forked over lightly, if needed. After the second day the malt should be turned at frequent intervals. In the modern type of kiln the drying process from the time of going on to coming off kiln usually occupies three days, and is distributed as follows:—

1st	day	not below	80°	or above	100°F.
2nd	,,	,,	100°	,,	130°
3rd	,,	,,	130°	,,	200°

The malt is not turned until the second day. As soon as the green malt is loaded on the kiln, the fan is started rapidly, and by this means a strong upward draught is induced which draws the moisture rapidly from the malt; as the latter becomes dry, the temperature is increased, and the speed of the fan is reduced. Medium and high-dried malts are finished off at much higher temperatures, ranging from 200° to 230° and upwards.

As soon as the temperature gets up to the final point, this heat is in a great many maltings maintained only for one or two hours. This is a great mistake; there can be no doubt that the longer the malt is exposed to a high heat, the sounder and better keeping will be the resulting beer. The final heat might certainly be attained in a shorter time than it usually is, and the malt might be exposed to this heat for at least 6 hours without undergoing any darkening in colour whatever.

Much the same method is pursued in the drying of the malt on double-floor kilns as on single. The malt is first loaded on to the top floor, where it is kept at a temperature not exceeding 120° until about 90 p.c. of the moisture is driven off. It is then dropped through doors or holes to the lower floor, where it is finally dried off at a temperature of from 180° to 190° or more, and the same heat and air that effect this are in fact the very best possible to drive off the moisture from the upper floor, which in the mean time will have been loaded with a fresh piece.

It is hardly necessary to say that in the process of kilndrying, where the temperature is the important factor, several thermometers placed on each floor are absolutely indispensable.

The malt, after it is finished drying, has yet to be freed from the radicles or 'combes.' This used to be accomplished in the old maltings by its being well trodden by men furnished with heavy-soled boots; the radicles being thus detached from the corns, and by passing the malt over a 'water-fall' malt screen it was completely freed from these as well as from some of the adhering dust. In modern maltings, as soon as the malt is thrown off the kiln, it is passed through a brushing machine, each kernel being brushed free from 'combes' and adhering dust. In some maltings, previous to being brushed, the malt is heaped up in the centre of the floor and remains so overnight with the fire well banked up.

We may get a very fair idea of the temperature at which the malt has been dried by observing the colour of the combes. The higher the temperature, the more highly coloured they become; indeed, where it is almost impossible to observe any difference in the colour of two malts dried at different temperatures, an examination of the combes from these malts shows it at once.

21. **Storing.** After freeing from the combes by screening, malt is usually stored away in bins for some weeks previous to use in the brewery. The floor, sides, and top of these bins should be made of good seasoned wood and lined with sheet zinc. These bins are usually built in the driest part of the malthouse; this would naturally be in the neighbourhood of the kiln, and it should be protected as much as possible from draughts.

During this storage of the malt previous to use some change certainly takes place in its nitrogenous constituents; in technical language, 'the fire is taken out of it and the malt becomes mellow,' but, whatever these changes are, nothing is known about them up to the present. All that can be said is that it has been found decidedly unadvisable to use any malt for brewing purposes until it has been stored for at least six weeks from the time of coming off the kiln.

22. **Characteristics of malt.** The following are the characteristics of a good malt, as given by Stopes:—

(1) *Growth.* The malt should be evenly grown, the acrospire showing between two-thirds to three-fourths up the back; any malt which contains many corns showing the acrospire protruding should be rejected. On the other hand,

it should also not contain more than 4 p.c. of ungerminated corns.

(2) *Slackness or moisture.* This will vary to a slight extent with the age of the malt, but on the average, malt should not contain more than 3 p.c. of moisture.

(3) *Age.* Malt is at its best from six weeks to four months; after that time, under ordinary conditions of storage, it gradually absorbs moisture and becomes more or less slack.

(4) *Odour.* Good malt should have a pleasant, well-known aroma peculiar to itself.

(5) *Condition.* This will depend a good deal upon the quality of the barley. Good barley badly managed may produce a bad malt, but a bad barley will never produce a good malt. Good malt should be tender and friable when broken, and should bite crisp and crumble readily under the teeth.

(6) *Cleanliness.* Malt should be comparatively free from mould and dust as well as rootlets and inorganic refuse.

7. *Flavour.* The flavour of malt is derived from influences of growth and of drying; it should possess a pleasant, mellow, sweetish taste, free from rawness on the one hand, and bitterness on the other.

Such are the characteristics of a good malt so far as can be determined by the eye, but these should always be supplemented by a complete chemical analysis.[1] By this means we obtain the following information:—

I. Actual composition:
- *a.* Starch products, as dextrin and maltose.
- *b.* Cane sugar.
- *c.* Other sugars.
- *d.* Total albuminoids soluble after boiling.
- *e.* Ash.
- *f.* Moisture.
- *g.* Insoluble matters or grains.

II. Relative diastatic capacity.

III. Specific rotatory power.

A brewer ought to have a fair idea of the constituents of his malt before commencing to mash with it, for from such an analysis as given above he will be in a position to predicate very fairly what kind of wort and beer his malt is going to produce, and so be enabled to control not only his mashing process, but all subsequent operations.

Other descriptions of malt, in addition to the kind we have hitherto been considering, are made and used. These are:

Brown or porter malt.

Amber malt.

Black, roasted, chocolate, or patent malt.

Brown and amber malt are prepared practically in the same way as ordinary malt until they go on kiln. Here they are dried at a much higher temperature, and wood is largely used for the purpose instead of coal or coke.

Black malt is simply ordinary malt which is roasted in exactly the same way as coffee berries are. 'A sample of properly roasted malt is uniform in colour, of a chocolate hue, not black, and each corn clear and clean. If it is black, with the corns burst, and especially if matted or run together, it is of a most inferior kind, and neither good flavour nor permanent colouring can be expected from it.'

[1] For full details of latest methods of analyses of malt, worts, and beer, *v.* Sugar, Saccharimetry.

23. **Malt adjuncts.** These may be divided into two classes. First, those substances from which the extract has to be obtained by the mashing process; and second, those in which the extract is already formed.

Class I. Several grains of cereals other than barley have been prepared for brewing purposes, either by malting or subjecting to the action of heat in some way or other. The principal of these which are at present used as substitutes for malt, either in a prepared form or in the raw state, are maize malt, germless maize, gelatinised maize, gelatinised rice, torrefied grain or white malt, and in the raw state barley, rice, and maize. When using any of these substances for brewing purposes, certain proportions of them are either mixed with the malt in the mash tun, or else the starch contained in them is first gelatinised in a separate vessel and rendered soluble by the addition of a little malt, and afterwards added to or sparged over the goods in the mash tun.

Class II. Under this head are included ordinary cane sugar, invert sugar, glucose or starch sugar, and dextrin-maltose.

Raw cane sugar cannot be recommended as a brewing material, owing to the large quantities of impurities of a dangerous character which are always present.

Refined cane sugar is used to a certain extent, but before it can undergo fermentation it has first to be hydrated or inverted by a peculiar unorganised ferment contained in the yeast and termed invertase, and as this reaction tends to weaken the yeast to a certain extent as well as favour the production of lactic acid, it has been found more advantageous to use cane sugar which has been previously inverted. This is done by means of sulphuric acid, which is afterwards neutralised with calcium carbonate, and the inverted sugar freed from the calcium sulphate by filtration is further purified by being passed over animal charcoal, and then boiled down under diminished pressure to a thick syrup, in which state it is sent out by the manufacturer.

24. **Hops.** The hop plant belongs to the nettle family, and is a perennial climbing or rather twining plant. It is found in the wild state all over Europe, and is propagated not by seed but by sets or suckers thrown up from the root, which is perennial, the stems dying down at the approach of winter, and fresh ones coming up each spring, and often attaining a height of 30 feet or even more. The hop plant bears two distinct kinds of flowers, male and female, and these flowers again are produced on distinct plants; of these only the plant bearing female flowers is cultivated, the male plant being rigidly excluded from most hop plantations. The flowers, which are the only parts of the plant of any use to the brewer, occur in the form of peduncles or cones, consisting of a series of scales or carpels lying above each other so as to form a cone. On the inner side and on the lower edge the carpel is turned over and encloses at first the female flower and afterwards the fruit developed from the flower. The fruits of the hop are round hard granules or little nuts; these fruits and the inner sides of the scales are thickly covered with a fine yellow dust—the so-called lupulin. Under the microscope this dust

is seen to consist of numberless granules, these granules being composed of glands, which are formed by the union of several simple cells. These glands are hollow, and this hollow space is filled with hop oil, resin, bitter principle, &c.

As a rule, the value of the hop may roughly be determined by the quantity of lupulin it contains.

In practice the quantity of the hop flour present — the 'condition,' as it is called — is roughly estimated by rubbing the hops between the hands, the amount of stickiness left forming an index as to the quantity of lupulin present in the hops.

Hops are principally cultivated in the counties of Kent, Surrey, Sussex, and Worcester. The Kent hops are in much repute, and more especially that variety known as Golding, being rich and delicate in flavour; the Sussex hops are somewhat coarser in flavour than Kent, and perhaps do not present such a pleasing appearance to the eye, but nevertheless are good useful hops for running beers or for mixing with Kents for higher-class ales.

Worcester hops are milder than the above, and in some breweries much preferred to any other. Of late years bad seasons and the attack of the hop aphis have done much to deteriorate the quality of English hops, so that at present large quantities are imported from Germany and America; but foreign hops lack that delicate aroma and flavour peculiar to English growth, and are as a rule only used for the lower quality beers. Hops, in order to be kept for any appreciable time, require to be thoroughly dried; the hop cones, after they are picked, are spread out on the floor of a kiln, where they are dried by artificial heat. Sulphur is often sprinkled on the kiln fires, and the sulphurous acid gas thus produced passing through the hops bleaches them, so that hops naturally dark in colour or unsightly in appearance are rendered more pleasing to the eye and fetch a higher price. Thausing claims that it is decidedly beneficial to subject hops to the sulphuring process on the kiln; but, unless where the mildew and other parasitic diseases have made their appearance, sulphuring is decidedly injurious as well as encourages fraud. On the other hand, it seems to be a pretty general custom nowadays to sprinkle the hop plants whilst growing with flowers of sulphur, to prevent or destroy certain diseases which attack the plants at various stages of their growth—such as mildew and blight—but it is evident that very little of this is to be found on the hop cones after picking; but even if any should remain adherent, being present as free sulphur, it can have little or no effect on the constituent principles of the hop.

In order to estimate the value of hops without having recourse to analysis, the following physical features may be taken into consideration: the fineness of the aroma, the proportion of lupulin which the cones contain, the proportion of stalk, seeds, and impurities which accompany the hops, and the general appearance of the cones themselves.

The following experiments (J. Inst. Brewing, xii. 301) were undertaken some years ago by the writer, with a view to getting some definite idea of the action of the various salts occurring in brewing waters upon hops. Both as regards the extractive properties of these salts as well as the flavour and colour of the extract so obtained, several experiments were made, of which the mean value is given in the annexed table. The method of experiment was as follows: The dry salts were added to distilled water at the rate of 21 grains per gallon, or 0·3 gram per litre; 10 grams of hops were then digested with 900 c.c. of each solution in a boiling water-bath, for one hour, cooled down to ordinary temperature, and made up to 1005 c.c. (10 grams of hops being found to be equivalent in bulk to 5 c.c. of water), shaken well up and filtered as bright as possible; 100 c.c. contained the extract of 1 gram of hops. This quantity was evaporated to dryness, dried in water-oven and weighed until constant, then ignited and weighed again; the latter weight subtracted from the former gave the weight of organic matter extracted from 1 gram of hops (J. Inst. Brewing, xii. 300).

Name of salt	Extract, per cent.	Colour in 4-inch cell. Total units	Analysis of colour		Flavour
			Red	Yellow	
Sodium chloride . .	18	7·2	1·2	6·0	Pleasant.
Calcium chloride . .	17	5·7	1·2	4·5	,,
Sodium sulphate . .	16	6·8	1·3	5·5	Rank.
Potassium sulphate . .	16	—	—	—	Harsh.
Magnesium sulphate .	16	6·2	1·2	5·0	Pleasant.
Calcium sulphate . .	17	6·5	1·5	5·0	,,
Sodium carbonate . .	19	10·9	1·9	9·0	Nauseous.
Potassium carbonate .	18	11·6	2·6	9·0	,,
Calcium carbonate . .	18	11·2	2·8	8·4	,,
Distilled water . .	20	4·7	1·1	3·6	Pleasant.

25. Chemical composition of hops. Hops contain, besides cellulose, woody fibre, water, and ash, certain substances, more or less soluble in boiling water, and which give an agreeable bitter and aromatic flavour to beer. These consist of hop oil, resins, bitter substance, and tannin.

The hop oil is an essential oil, giving to the hop its characteristic agreeable smell. It is present to the extent of about 0·8 p.c. in the glands of the hop cone, and may be obtained by distillation in a current of steam, the volatile oil floating upon the surface of the condensed water in the receiver, from which it may be

separated by decantation. During the boiling of the hops with the wort in the copper the greater portion, if not all, of this oil becomes volatilised and lost to the brewer; hence a process has been recently introduced for extracting this oil from the hops previous to boiling, and afterwards adding it either to the wort before ordinary fermentation or to the finished beer.

When obtained from fresh hops, the oil has a light-yellow colour, hot burning taste, and agreeable aromatic smell. It is only slightly soluble in water, but freely so in alcohol, ether, and light petroleum. Not only is the hop oil volatilised at temperature of boiling water, but also slowly at ordinary temperatures and by exposure to air is easily oxidised into volatile acids, especially valerianic acid, to the presence of which the peculiar odour found in old hops is due.

A. C. Chapman has investigated the composition of hop oil and has found it to consist principally of *myrcene* and a sesquitespene which he has termed *humulene*, together with small quantities of *linolool* and *linalyl isononoate*.

This hop oil is generally found intimately mixed with resin, which it seems to be capable of dissolving to a certain extent. It seems very probable that the resins of the hop (three of which have been determined) are the results of the oxidation on the one hand of the hop oil, and on the other of an organic acid. Bungener (Bull. Soc. chim. 45, 9), who has isolated it from hops and studied its properties, has termed it *lupulinic acid*. Hayduck (Wochenschrift für Brauerei, 1887, 347) has detected three different resins in hops—one a soft resin, precipitable by lead acetate and soluble in petroleum ether; a second, also soft resin, soluble in petroleum ether, but not precipitable by lead acetate; and a third one, hard and solid, not soluble in petroleum ether and not precipitable by lead acetate. Experiments made by Hayduck show that the second of these resins is identical with the soft resin formed by the oxidation of Bungener's *lupulinic acid*, whilst the third resin is due to the oxidation of hop oil. Hayduck also shows that the soft resins possess highly antiseptic properties, whilst the hard one checks to a certain extent the rapidity of fermentation. It was found that when these resins were repeatedly extracted with water the aqueous solution gradually decreased in antiseptic power; this tends to show that it is inadvisable to boil hops more than once, since the first boiling would probably extract the greater portion of the soft and more soluble resin.

Although it is possible to estimate with a fair degree of precision the various constituents of hops, it has not been so far found possible to establish any very definite relation between the value of the hops and the amount of essential oil, resins, and tannin which they contain. Consequently, up to the present time, chemistry has not afforded much assistance in this direction. Briant and Meacham (Jour. Fed. Inst. Brewing, 1897, 2, 233) have proposed a method for the valuation of the preservative power of hops which consists in estimating the amount of soft resin they contain. Heron proposed to estimate the value of hops by the amount of tannin they contain. He considers that the larger this amount is the better the sample. Barth (Zeit. f. d. Gerammt Brauwerein, 1897, 168) confirms this view to a certain extent. He finds that all good hops contain high percentages of tannin.

Diastase of hops.—Hops, like all other plants, contain diastase, but this point appears to have been overlooked until attention was called to the fact by Brown and Morris (Trans. Inst. Brewing, 1893, 94).

The tannic acid which occurs in hops is a fawn-coloured powder, easily soluble in water and weak alcohol, but insoluble in ether. In aqueous solution it gives a dark-green colouration with ferric chloride, and possesses the property of precipitating in flocks the albuminous bodies of malt wort. It is therefore an eminently useful substance in the manufacture of beer. From the foregoing it would appear that the only substances in hops of any use to the brewer are the soft resins and tannic acid. These soft resins are readily oxidised into the hard and insoluble variety, whilst tannic acid is capable of being converted in like manner into gallic acid, a substance possessing very few of the properties of tannic acid. It is not, then, a matter of surprise that old hops are of little or no value, for considering the loose manner in which they are housed in most breweries, subject to every variation of temperature and freely exposed to the air, changes in the composition of the active principles must of necessity take place in a more or less rapid time, rendering them eventually of little or no value to the brewer.

Briant and Meacham (Jour. Fed. Inst. Brewing, 1897, 3, 487) have described numerous experiments which they had conducted to discover the best method of storing hops. They recommend the use of a cold chamber at a temperature of 36° to 40°F.

This method of storing has been proved to give excellent results, and has been very generally adopted throughout the trade.

26. **Yeast and fermentation.** Before the classical researches of Pasteur, various theories were advanced to account for the phenomena connected with fermentation, but he was the first chemist who proved that the process of fermentation was due, not to a peculiar protoplasmic substance secreted by the yeast fungus, but that the presence of the plant itself in the saccharine liquid is essential to alcoholic fermentation, and that the yeast cells have the power, in the absence of the oxygen of the air, of splitting up sugar into alcohol and carbonic acid, and deriving the oxygen necessary for their support and nourishment by that means.

Pasteur has shown that easily fermented saccharine solutions can remain for years without decomposing, even when the air has access to them, provided that the living germs which were originally present in those solutions be first destroyed by heat, and that care be taken not to let any but absolutely pure, that is, germ-free air enter those solutions afterwards. But the moment impure air was allowed to enter the liquid, or the minutest portion of living yeast, fermentation was rapidly set up.

Pasteur has also shown that associated with ordinary yeast are to be found in most fermentations and beers a great number of organisms of quite a different appearance and character to yeast cells, and which may all be classed under

the general term of bacteria, and he proved most conclusively that these organisms are capable of and do give rise to the various diseases to which beer is subject. Or in other words, that, in addition to the healthy fermentation of saccharine solutions carried on by sound yeast, these other organisms, if present, are also capable under certain conditions of carrying on fermentations which give rise to products other than alcohol and carbonic acid. Hence these bacteria or false ferments have been classified and named according to the functions they fulfil or the products they give rise to.

Those organisms which induce alcoholic fermentations in a saccharine solution are known under the general name of saccharomyces, and since under normal conditions they reproduce themselves by gemmation or budding, they have been assigned to that division of the great fungus group known as budding fungi. In brewing technology they are known under the general term 'yeast.' Yeast cells are either single or occur in groups or strings; each cell consists of a thin-walled sac or bag containing a semi-fluid matter, in the centre of which there is often a space full of a more clear and watery fluid than the rest, which is termed a vacuole. The sac is comparatively tough, but it may easily be burst, when it gives exit to its contents, which readily diffuse themselves through the surrounding fluid. The whole structure is called a cell, the sac being the cell wall and the contents the protoplasm. Under a high magnifying power each cell is seen to be round or oval, and on the average about $\frac{1}{3000}$ inch in diameter. An agglomeration of such cells is technically termed 'yeast,' and to the naked eye appears as a thick, slimy cream-coloured fluid, from which all the moisture can be pressed, and the residue dried at a low temperature to a powdery mass without losing its vitality; but if heated in the moist state to the temperature of boiling water, its fermentative power is completely destroyed. Fermentation which has already commenced in a saccharine liquid can be stopped by boiling it.

When a minute quantity of yeast is added to some malt wort which has previously been filtered bright, and is then kept in a glass flask at a temperature of about 70°F., after a few hours bubbles of gas will be seen to rise to the surface of the liquid, which gradually becomes more and more turbid, and later on a sediment will be observed at the bottom of the flask or a scum may collect at the surface, carbonic acid gas being copiously evolved. If the yeast cells be carefully examined under the microscope from time to time whilst this is going on, it will be noticed that at first the vacuoles which were present in every cell gradually disappear, each cell becoming full and rounded in appearance owing to the absorption through its cell wall of certain nourishing substances from the wort. Soon minute little buds will be noticed jutting out from the sides of the cells; these buds rapidly grow and soon assume the size of the parent cell, from which they finally become detached, but not before they in their turn have developed other buds, and these yet others, thus giving rise to those groups or strings of cells which are sometimes seen under the microscope. This cell reproduction and growth is due, then, to the nourishment which the yeast derives from the wort, but for some time after the yeast cell continues to produce any buds, and even after the rupture takes place between the parent cells and the resulting daughter cells, the former still continue to absorb various substances from the liquid. This may be looked upon as a kind of fattening process, and is due to the assimilation by the yeast of certain nitrogenous matters contained in the worts. Hence the process of fermentation of malt worts may be regarded as first an absorption of carbohydrate substance by the yeast cell, the transformation of this substance into alcohol and carbonic acid, whilst at the same time the oxygen derived from this decomposition enables the yeast cell to thrive and grow and to put forth buds.

When this period of growth is accomplished, a fattening of the cells takes place at the expense of the nitrogenous bodies readily assimilable by yeast and which consist principally of amido- and amino- acids (asparagin, trypsin and leucine); if no assimilable nitrogen be present this fattening does not take place, and the yeast becomes starved, as it were, and perishes; if, on the other hand, there be a large excess of these nitrogenous matters in the worts, the yeast cells become overfed, and their capacity for reproduction considerably diminished, for it has been found that the power of multiplication and the formation of new cells *decreases* with the *increase* of nitrogen in the yeast.

It is essential, therefore, that the brewer obtains a wort which is both constant in quality and definite in composition, and which exactly suits the type of yeast he employs.' For a type is produced by environment, and varies as the composition of the wort varies.

A wort produced entirely from malt contains a large excess of assimilable nitrogenous substances, and is hardly an ideal medium for yeast production and vitality. It is found advantageous to 'dilute' these nitrogenous bodies with a certain proportion of material devoid of yeast nutriment. Raw or gelatinised grain, invert sugar, glucose or other similar brewing sugars are used for this purpose. A very satisfactory grist is composed of the following proportions: 60–65 p.c. malt, 18–22 p.c. brewing sugar and 13–18 p.c. unmalted cereal.

Among the factors which exert a considerable influence on the progress of fermentation, besides that of the chemical composition of the liquid, temperature and the amount of oxygen present in the liquid may be mentioned. This much is known of the effect of oxygen on the progress of brewing in practice, that in order to get a good result it is a necessity to aërate the wort, *i.e.* to let it take up oxygen from the air. Pasteur's researches on this subject led him to state that fermentation is life without air, and that yeast can only decompose sugar by taking the necessary oxygen from the sugar molecule. His theory has, however, proved to be wrong. A deeper insight into the influence of aëration on fermentation in breweries could only be obtained by the study of pure culture species and races, for, as Hansen's investigations in brewing practice have shown, they behave differently with respect to oxygen. Hansen found further that when the yeast cells have free access to the oxygen of the air they can yet produce an active fermentation, an observation

which contradicted the theory of Pasteur. Adrian J. Brown observed that a plentiful supply of oxygen increases the fermentative activity of the single cell, even when the cells are in such circumstances as prevent multiplication (Chem. Soc. Trans. 1892, 1894).

Not only has Pasteur established the fact that fermentation is due to the development and growth of yeast in saccharine solutions, but he has also shown that there are several distinct species of yeast, each one differing from the other in functions and properties, and of the several species which are capable of inducing alcoholic fermentation he identified the following as being present in malt worts, in addition to that species known as *Saccharomyces cerevisiæ*, the true beer ferment, *Saccharomyces pastorianus*, *S. ellipsoideus*, *S. exiguus*, and *S. apiculatus*. These he found were always present in the atmosphere as well as on the surface of all fruits, so that if some sweet wort be freely exposed to the air, it will in the course of a few hours manifest all the signs of alcoholic fermentation; but, in addition to these various species of yeast, spores of bacteria and moulds will also manifest themselves and develop, so that after a few days, if left to itself, this wort becomes quite turbid, is covered with a thin film, emits a disagreeable smell, and soon putrefies. Hence the necessity for boiling the wort before fermentation; by this means all the spores which may have been present, derived in great part from the surface of barley or malt, are killed and the wort rendered free from all foreign germs, and ready to undergo a true yeast fermentation.

But although Pasteur directed attention to the presence of these other forms of saccharomyces or wild yeasts, as they are now termed, in fermenting worts and beer, he did not tell us how to introduce into the liquid about to be fermented a seed yeast which is really free from all such forms of wild yeast. This work was reserved for Hansen, and was brought to a most successful issue by him. He started with the idea of cultivating a crop of yeast from a single selected yeast cell, and pure yeast thus procured was first used for brewing purposes at old Carlsberg Brewery, near Copenhagen, in 1883 (Meddelelser fra Carlsberg Laboratoriet, 1881). In that year he brought forward his doctrine that some of the most dangerous and most common diseases of low fermentation beer were caused, not by bacteria, but by certain species of saccharomyces, and that each of the names employed by Rees—*S. cerevisiæ*, *S. pastorianus*, *S. ellopsoideus*—represented not one but several kinds or races. He showed that varieties which had been until then incorrectly grouped under the name of *Saccharomyces cerevisiæ* gave in the brewery products having quite different characters. Since then, carefully selected types of yeast from pure cultures on this method have been introduced into all the leading breweries of Denmark, Norway, and Bavaria, with the most marked success. So far, all the work that has been done with pure yeast relates to that particular variety which is employed on the Continent and known as bottom yeast, or low fermentation yeast, so called because the fermentation is there carried on at a low temperature (47°F. or even lower), and is a slow process extending over some weeks, during which the yeast sinks to the bottom of the vats or casks, in contradistinction to the English method of fermentation termed high fermentation, and the yeast, top yeast, because here the process is conducted at a high temperature commencing at about 60°F. and running up to 70°F. or more, so that the fermentation is much more rapid and the yeast thus produced rises to the surface and works out of the bungholes of the casks or is skimmed off the surface of the fermenting tuns.

A great deal of practical work has been done in the way of pure yeast cultivation on the large scale in English breweries with varying results. H. T. Brown and G. H. Morris carried through a series of experiments between the years 1885–94 in a large Burton brewery, but found that although the beers produced were sound, they hardly ever came into condition, and no secondary fermentation occurred, unless after the addition of malt extract or sugar priming. Later investigators have found that for many ales the system can be adopted with very satisfactory results, as they have found that in this type of beer, fermented with a single-cell yeast, a continuation of the primary fermentation occurs after racking and lasts for about a fortnight. It is conclusively proved that the true secondary fermentation, such as occurs in the case of stock ales when stored for a considerable period, is not brought about by primary yeast, and hence the failure of Hansen's system in the English breweries.

N. H. Claussen has studied the yeasts which bring about the secondary fermentation in English beers (J. Inst. Brewing, 1904, 10, 308), and has discovered a non-sporulating budding fungus belonging to the Torula group which possesses the special property of setting up secondary fermentation, and even creates in Continental beers that flavour and condition typical of English beers. He gives the name of Brettanomyces to this organism, and holds the belief that it is a constituent of the pitching yeast.

Sufficient has been done to prove that in ordinary brewery yeast the English brewers also possess a mixture from which, by Hansen's method, several varieties of *S. cerevisiæ* can be separated, which cannot microscopically be distinguished from each other, but which, when used upon a practical scale, give entirely different results, both as to flavour, brightening, attenuation, and mode of separation of the yeast. Experiments have also shown that these characteristics can be maintained unimpaired throughout a very great many successive fermentations in the brewery (Morris, J. Soc. Chem. Ind. 1887, 113).

Great differences have been found to exist in the fermentative capabilities with regard to different sugars. Most yeasts ferment glucose and fructose, but there are several types which are unable to ferment such sugars as maltose, cane sugar, and milk sugar. This difference is evidently dependent upon the enzyme which the yeast is able to secrete. It has long been known that cultivated yeast secretes an enzyme called *invertase*, which hydrolyses cane sugar, converting it into the more readily fermentable sugars dextrose and lævulose. It has more recently been found that these yeasts secrete another enzyme, *maltase*, which converts maltose

into glucose, previous to its fermentation. As long ago as 1858, Traube brought forward a theory relating to fermentation, which, however, received little credence at the time. According to this theory, fermentation is explained as an effect due to the various enzymes contained in yeast, and not to the yeast cell itself. This theory has been practically confirmed by the discoveries of Emil Fischer (Ber. 27, 1894 and 28, 1895) and Ed. Buchner. Fischer's investigations on enzymes have not only brought to light new facts, but have also pointed to quite new views as to the nature of the processes concerned. In 1897, Buchner, by submitting yeast to high pressure, succeeded in obtaining an extract capable of producing fermentation in solutions of sugar. He concluded from his experiments that the active element in the expressed juice was an enzyme which he called *zymase*. Its fermentative power he found to be several hundred times less than that of living yeast, and it loses its activity on keeping.

This activity is not influenced by yeast cells nor is this activity, when lost, restored by the action of living cells.

A very large amount of work has been done since 1897, as the direct result of the new series of investigations provided by Buchner's researches, both in England and abroad. A valuable resumé of these researches will be found in two papers read before the Institute of Brewing by Dr. Arthur Harden (J. Inst. Brew. 1905, 11, 2–15, and 1910, 7, 663–634) (*v.* FERMENTATION).

Hansen found that particular forms of disease which manifest themselves in beer after it has been stored in cask are due to the presence of species of wild yeast (Meddelelser fra Carlsberg Laboratoriet, 1883), and notably to certain varieties of *S. pastorianus*, but he has also shown that if these wild types are present to the extent of not more than 2·5 p.c. on the total quantity of yeast, they do not develop their particular form of disease. Brown and Morris (Non-crystallisable Products of the Action of Diastase upon Starch, Chem. Soc. Trans. 1885, 569) have found that some of these 'wild types of yeast,' *S. pastorianus* and *S. ellipticus*, which with other species constitute the secondary ferments of our high-fermentation beers, are capable of first hydrolysing the dextrin to maltose and then fermenting it, and these results have been fully confirmed by the author on the large scale in the brewery. It is perfectly certain that the 'sick frets' and other diseases which prevail in summer-time amongst certain kinds of beer, are due to the presence in large quantity of these wild yeast types in the beer.

There are also present among the secondary ferments of our top-fermentation beers several types of the *Torula* group, one type of which has been investigated by Claussen, as already mentioned. By *Torula*, Hansen understands yeast cells which are similar to *Saccharomyces*, but do not form endospores nor develop typical mould growths. As regards the production of alcohol, they may exhibit this in all degrees. Comparatively little is known as yet with regard to these yeasts, but no doubt in the near future they will be more fully investigated.

A method for the preservation of yeast whereby it can be transported to foreign countries, has been patented by the writer. It simply consists of the admixture of ordinary pressed yeast with solid glucose. The glucose is first melted by heat and allowed to cool, when it does not immediately set, but remains liquid. The brewer's yeast is first pressed and then incorporated with it, when the whole mass sets hard in the course of a few hours; the yeast is thus, so to speak, imprisoned in the crystallised glucose, yet without being completely dried up, and retains its fermentative power with but slight diminution for a very long period.

As we have seen, the microscope does not enable us in some instances to differentiate one form of yeast from another, and in order to be able to do this some other method must be resorted to. It has long been noticed by many observers, more especially by Rees, Engel, and Brefeld, that under certain conditions the yeast cell, instead of throwing out a bud, multiplies itself in another way: its protoplasm divides itself into four masses termed ascospores, each of which surrounds itself with a cell wall, and the whole are set free by the dissolution of the cell wall of the parent.

Hansen found that the ordinary bottom-fermentation yeast only formed spores at 25°C. after some days, whilst the wild forms are capable of forming ascospores at this temperature in a few hours, and upon these results Holm and Poulsen (Meddelelser fra Carlsberg Laboratoriet, 1886) have based a method for the practical analysis of brewer's yeast. The method of procedure is as follows: A small quantity of the yeast to be examined is spread on a small sterilised block of plaster of Paris; this block is then placed in a flat covered glass dish and kept moist by water previously poured into the dish. This is then placed in the thermostat or forcing chamber, and kept at a temperature of 25°C. for forty hours. At the end of that time it is carefully examined under the microscope, when the spores, if any wild yeast be present, will be seen as round bodies within the cell wall.

Grove Johnson and S. Hare (J. Inst. Brewing, xi. 467), in the course of some bacteriological experiments, accidentally discovered a new yeast, to which they gave the name of *Saccharomyces thermantitonum*, owing to its power of resisting high temperatures. It proved to be a true yeast, forming spores at definite temperatures and capable of setting up a vigorous alcoholic fermentation in a saccharine solution at a temperature of 110°–130°F. Prof. Lindner states that this new yeast differs from Logos yeast in that it precipitates in a much more compact mass. He further states that at 109°F. the fermentation proceeds quickly and normally, and the yeast retains its ability to isolate itself in large lumps, thereby causing a spontaneous clarification of the wort.

Yeast has always been classified as belonging to the fungoid group of plants, but those other organisms which also have the power of inducing fermentation other than alcoholic in saccharine solutions, have been regarded by the older observers as belonging rather to the animal than to the vegetable kingdom, chiefly on account of their motility and in the absence of the basis required for a more exact comparison, but later investigators see no reason for separating them from the vegetable kingdom, although all

that can yet be said of them is that they may be classed as bacteria, and 'are a group of simple plants of a low order.'

Of these the species best known to us as occurring in beer are *Saccharobacillus pastorianus, Bacillus amylobacter, Bacterium termo, Bacterium aceti, Bacterium lactis,* and *Sarcina.* There are other species of which little is known, but which are often met with in old beer, such as the ropy ferment, colour bacterium, certain forms of *vibrio, spirillum,* &c.

These constitute what are known as the disease germs of beer, and generally develop under favourable conditions in the finished beer after it has been some time in cask or bottle. *Bacterium aceti* has the power of converting the alcohol of the beer into acetic acid; *B. lactis* attacks the saccharine matter, converting it into lactic acid; whilst butyric acid is supposed to be derived from the further fermentation of lactic acid by means of *Bacillus amylobacter,* or from sugar along with butyl alcohol by means of the same organism. These three forms of bacteria are perhaps those most commonly occurring in beer.

A few forms of mould are sometimes met with, such as *Mucor racemosus, Penicillium glaucum, Aspergillus niger*; but space will not permit to treat further of this subject.

Energy of fermentation.—Leaving out of consideration the different physiological conditions of the yeast, the various races show marked differences in their fermentative activity. This can be estimated by observing the amount of gas evolved in a given time. The apparatus shown in Fig. 9 is used for the purpose, and

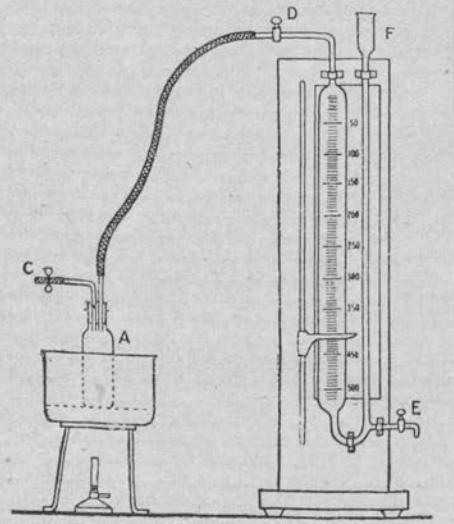


FIG. 9.

consists of a flask, A, containing the yeast and a solution of cane sugar. It is placed in a water-bath provided with a perforated false bottom, the contents of the bath being kept at a constant temperature of 86°F. The flask A is furnished with an indiarubber cork having two perforations, into each of which short pieces of glass tube are inserted. To one of these the tube communicating with the measuring apparatus is connected, to the other a stout piece of india-rubber tube which can be closed by an ordinary burette clip. The measuring apparatus consists of a U-shaped tube, one limb which is considerably wider than the other, is constructed to hold 500 c.c. and is graduated into 10 c.c. divisions. The extremity of the narrower tube carries a funnel-like expansion, and is provided at its lower end with a tap; the upper extremity of the wider limb carries a narrow tube bent at a right angle, and also a tap.

When a determination is made, 10 grams of yeast under examination are intimately mixed with 400 c.c. of a 10 p.c. solution of cane sugar, and introduced into the flask. This is then placed in the water-bath, which has been previously heated to and is now constantly maintained at a temperature of 86°F. and is allowed to remain uncorked for an hour; in the mean time the measuring apparatus is made ready. Five c.c. of paraffin oil are first poured into the funnel, and afterwards water. This latter drives the oil before it, and this, when it enters the measuring chamber, floats on the surface of the water and prevents the absorption of carbonic dioxide. Sufficient water is then introduced to bring the surface of the paraffin layer to the zero mark on the scale. After the flask has stood for an hour in the water-bath, the apparatus is connected up, the tube C being left open while this is being done. This is now closed with the clip, the tap D opened, and the time noted as fermentation proceeds. The disengaged gas gradually displaces the liquid in the wider limit, and the tap E is opened just sufficiently to allow the water to escape at the same rate as the gas enters. At the expiration of half an hour, the taps D and E are closed, the clip C is removed, and with the assistance of the pointer the level of the liquid in the two limbs adjusted to the same height, either by pouring water into the funnel or drawing it off by the tap A, and the quantity of collected gas read off.

27. Having very briefly glanced at the different materials used in brewing, we proceed next to consider the various processes involved in the manufacture of beer.

Preparation of malt for mashing. As soon as the malt is delivered at the brewery it is further cleaned by screening from adherent dust, mould spores, and small corns. It is then delivered into a small hopper, from which it passes to the malt mill. This consists of a pair of smooth steel rollers, or, preferably, of two pairs of such rollers, one pair of rollers being set to a wider gauge than the other. When passing through such a set of rollers the larger corns are crushed by that pair which is set so as to crush them sufficiently but not too much, whilst the smaller corns pass on to the other pair, which are set at a narrower gauge so as to ensure the complete crushing of every individual corn. By this means a comparatively even grist is obtained. As the malt is ground it passes to the grist case (C, Fig. 10) which is generally placed over or has command of the mash tun.

The grist case should be made of well-seasoned pine or deal, planed smooth and well jointed, and should be lined with sheet zinc, or it may be constructed of galvanised iron. The bottom of the grist case must be of sufficient

slope to allow of the grist falling easily and readily into the mashing machine, and is provided at the bottom with a sliding valve.

28. **Mashing process.** From the grist case the crushed malt passes on to the outside mashing machine, where it meets with the mashing liquor at a temperature varying, according to circumstances, from 160°F. to 170°F. The malt and water are here thoroughly mixed before running into the mash tun. The best form of machine for this purpose, and the one most generally employed, is Steel's masher, of which a section is shown at Fig. 10, D. This consists of a horizontal cylinder closed at one end and open at the other, from 3 to 6 feet in length and from 8 to 22 inches in diameter. It is fixed horizontally above the level of the upper edge of the mash tun, and is usually furnished with a shoot whereby the mash may be conducted into one or more tuns. For instance, where two mash tuns are employed, the steel masher is fixed between the two tuns in such a way that it can be used for either one at pleasure. Inside the cylinder and running its whole length is a shaft provided with spokes at short and regular intervals, and of such a length that they just revolve freely inside the cylinder as shown in section.

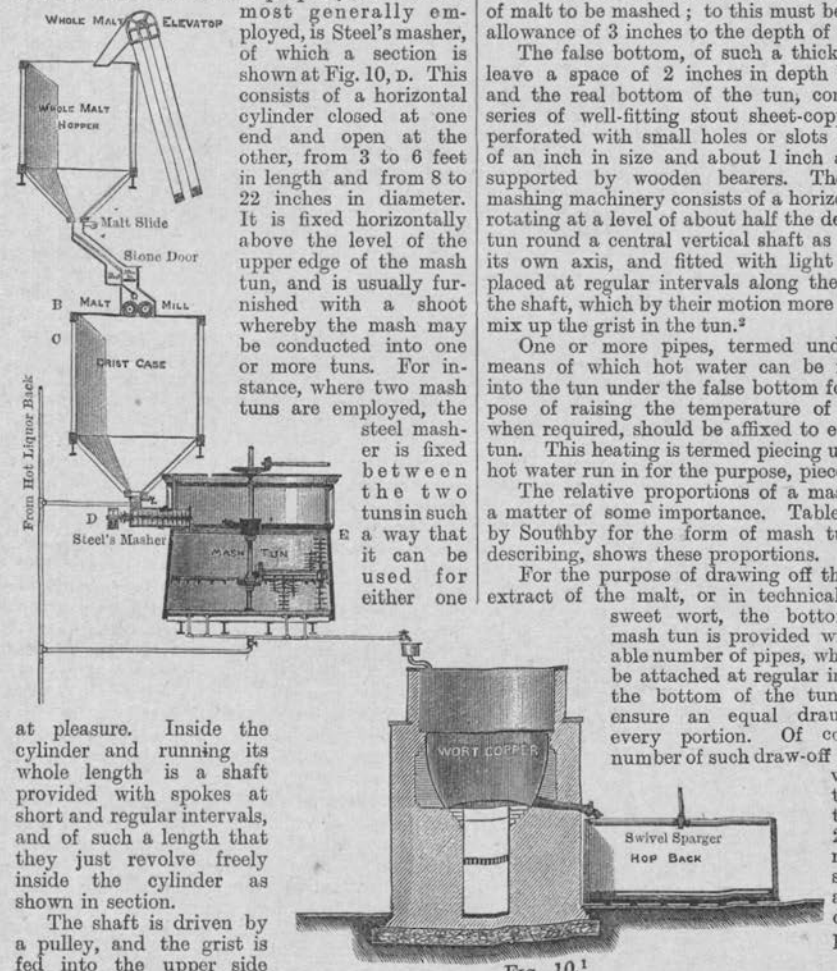


Fig. 10.[1]

The shaft is driven by a pulley, and the grist is fed into the upper side through the upright T-piece, the water from the hot liquor back meeting the grist at this point.

A slide, accurately adjusted by means of a screw, regulates the fall of the malt, whilst a screw tap allows of the admission of the proper quantity of water.

The process of mashing is carried on in a vessel called a mash tun, E. This may be made of wood, wood lined with copper, or of iron, but the material most generally employed is iron, as it is found to last very much longer than wood and is more easily cleaned. Wood mash tuns, when used, are constructed of staves of best English oak, with a bottom of Dantzic fir. The staves should not be less than two and a half inches thick for small tuns, which must be increased for larger tuns in proportion to their size. The mash tun is provided with a false bottom, an internal mashing machine, and a pipe, termed an underlet, for introducing hot liquor from the main into the mash tun when desired. The capacity of the tun should be such as to allow three and a half barrels for every quarter of malt to be mashed; to this must be added an allowance of 3 inches to the depth of the tun.

The false bottom, of such a thickness as to leave a space of 2 inches in depth between it and the real bottom of the tun, consists of a series of well-fitting stout sheet-copper plates perforated with small holes or slots one-eighth of an inch in size and about 1 inch apart, and supported by wooden bearers. The internal mashing machinery consists of a horizontal shaft rotating at a level of about half the depth of the tun round a central vertical shaft as well as on its own axis, and fitted with light iron bars placed at regular intervals along the length of the shaft, which by their motion more effectually mix up the grist in the tun.[2]

One or more pipes, termed underlets, by means of which hot water can be introduced into the tun under the false bottom for the purpose of raising the temperature of the mash when required, should be affixed to every mash tun. This heating is termed piecing up, and the hot water run in for the purpose, piece liquor.

The relative proportions of a mash tun are a matter of some importance. Table V., given by Southby for the form of mash tun we are describing, shows these proportions.

For the purpose of drawing off the aqueous extract of the malt, or in technical language sweet wort, the bottom of the mash tun is provided with a suitable number of pipes, which should be attached at regular intervals to the bottom of the tun so as to ensure an equal draught from every portion. Of course, the number of such draw-off pipes must vary with the size of the tun. A 25-quarter mash tun should have at least six draw-off pipes. The mash

Table V.

Quarters of malt mashed	Diameter of tun	Depth of tun	Quarters of malt mashed	Diameter of tun	Depth of tun
	ft. in.	ft. in.		ft. in.	ft. in.
	5 2	5 1	25	10 2	6 5
5	6 4	5 5	30	11 0	6 6
8	7 0	5 6	40	12 6	6 9
10	7 7	5 8	50	13 9	7 0
12	8 4	5 10	75	16 3	7 6
15	9 4	6 1	100	18 1	8 0
20					

[1] For the drawings of brewery plant, the author is indebted to Mr. J. Oxley, brewers' engineer, Frome.

[2] For large mash tuns two such shafts are employed.

tun in all instances is provided with a cover. This should be carefully made and should fit well; it prevents the cooling of the mash and protects the surface of it from dust.

This cover may be of two forms, square top and conical, but the one to be most preferred is undoubtedly the conical. The square top, which is of the same diameter all the way up as the mash tun, and is from two to two and a half feet in height, is provided with doors or sliding shutters. The great objection to this form is the large amount of space left above the mash, and the facility afforded by the flat top for the collection of dust.

The conical cover is made in irregular sections, all of which are removable, whilst the objections to the square top are reduced to a minimum.

Both these types of covers, however, are being rapidly replaced by copper covers, generally hood-shaped, hung on chains, and worked by pulleys and weights so that the hood can be readily lowered or raised as desired.

The draw-off pipes to which taps are affixed are carried separately from the mash tun to a small receiving vessel termed the 'underback,' into which the wort from each tap flows, and is conveyed from this to the copper.

Figs. 11 and 12 give a general view of all the mashing arrangements described above.

As we have said, the malt as it leaves the grist case meets in Steel's mashing machine with the hot liquor, and both, thoroughly intermixed, are run into the mash tun. As soon as all the grist is run in, a few gallons of mashing liquor are run through the Steel's masher, and then the rakes are set going, two turns round

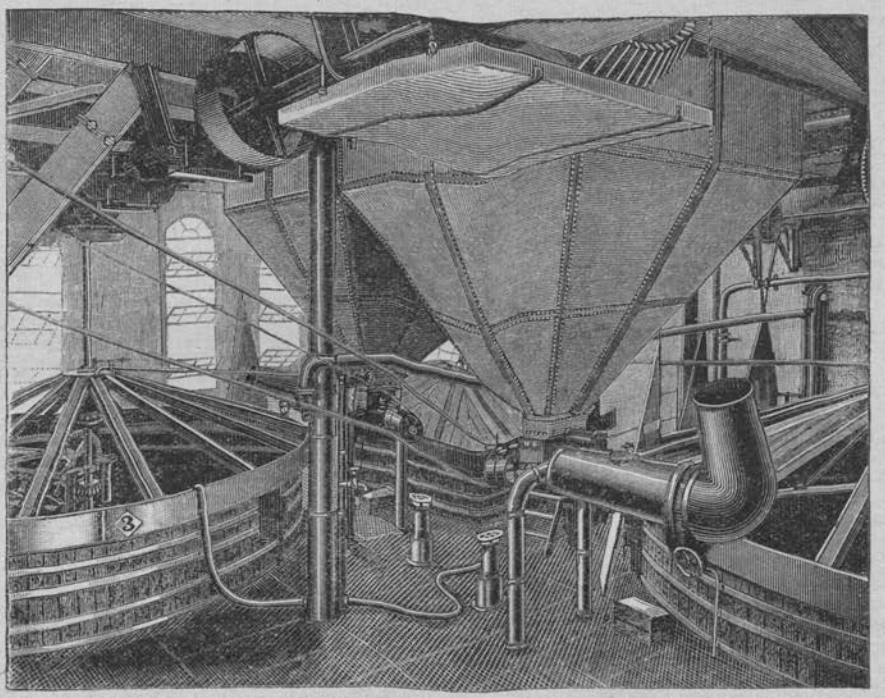


FIG. 11.—MASHING-ROOM IN MESSRS. WORTHINGTON & CO.'S BREWERY, BURTON-ON-TRENT.[1]

the tun being considered sufficient. The temperature of the mash is then taken; this may vary from 140°F. to 150°F. according to the practice of the brewery. If this initial temperature is not up to the proper point, then some more hot liquor is introduced through the underlet until the right temperature is attained; the covers are shut up and the mash allowed to stand, generally for one and a half to two hours.

29. **The chemical changes which occur during mashing.** When ground malt is brought into contact with water at the mashing temperature, the starch which it contains becomes gelatinised and the several enzymes present in the malt are enabled to perform their several functions. The amylo-hydrolyst or diastase acts upon the starch, which becomes rapidly converted into dextrin and maltose; the proteo-hydrolyst or proteolytic enzymes act upon the nitrogenous or albuminoid bodies, converting them into less complex and more soluble compounds, some of which are in a form readily assimilable by yeast. The other carbohydrates, such as dextrose, cane sugar, and lævulose (known as the ready-formed sugars of malt), also enter into solution.

The action of the proteolytic enzymes *peptase* and *tryptase* is practically a continuation of the action taking place on the growing floors during the process of malting, but is somewhat restricted, owing to the temperature of the mash being above the maximum of activity of these ferments. The action consists, as already pointed out earlier in this article, in the production of albumoses, peptones, and amides and

[1] This, with Fig. 15, are taken from Noted Breweries of Great Britain, by kind permission of Sir J. Causton & Sons.

amino-acids, the latter, the lowest type of nitrogenous bodies formed, being those most readily assimilated by yeast.

Recent researches have proved most conclusively that when gelatinised starch is acted upon by diastase it is split up into dextrin and maltose, and, under certain conditions, into maltodextrin as well, and that this change is a molecular one, and does not take place according to one equation, but to several, depending upon the temperature at which such a transformation is effected, and that the conversion afterwards of the dextrins first formed into maltose is a slow and gradual act of hydration. In all probability the molecular transformations of starch may be represented by at least eight possible equations, depending upon the temperature at which such transformations are effected.

The following table gives the respective proportions of maltose and dextrin corresponding to these eight equations, as well as the cupric-oxide reducing power K and specific rotatory power $[\alpha]_D$ (3·86 divisor), for the joint products of each of these transformations:—

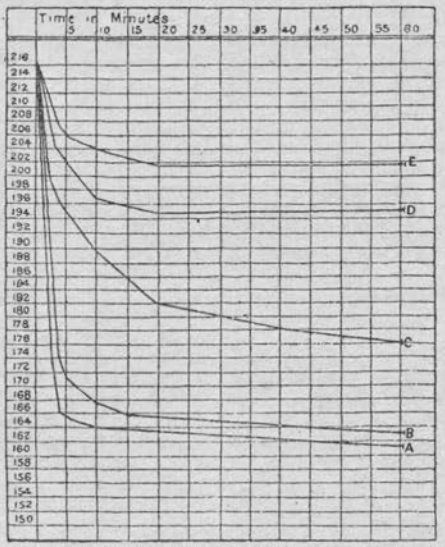
TABLE VI.

No. of transformation	Maltose	Dextrin	K	$[\alpha]_D$	Resulting dextrin
Soluble starch	0	0	0	195·0°	—
1	10·4	89·6	6·4	188·6	Erythro-dextrin α
2	20·8	79·2	12·7	182·4	,, β
3	31·0	69·0	18·9	176·2	Achroo-dextrin α
4	41·3	58·7	25·2	170·2	,, β
5	51·3	48·7	31·3	164·3	,, γ
6	61·1	38·9	37·3	158·4	,, δ
7	71·0	29·0	43·3	152·5	,, ε
8	80·8	19·2	49·3	146·7	,, ζ
9	90·3	9·7	55·1	141·0	,, η
Maltose	—	—	61·0	135·4	—

Throughout the whole range of the transformations of starch conducted with malt extract under the most varying conditions, results may be obtained which are always compatible with the hypothesis that the hydration and splitting up of the molecule of soluble starch are attended with the production of (1) a crystallisable body, maltose, having a specific rotatory power of $[\alpha]_D = 135·4°$, and a cupric-oxide reducing power of K=61; and (2) a series of non-crystallisable polymeric bodies, the dextrins, all having the same specific rotatory power of $[\alpha]_D = 195°$, and no cupric-oxide reducing power whatever.

The influence which temperature exerts upon the transformation is readily seen on referring to Table VII., where is shown a series of curves for transformations made under varying conditions of temperature, and taken from Brown and Heron's paper on the Transformations of Starch (Chem. Soc. Trans. 1879, 596). It is at once evident from these curves that the percentage of dextrin in any given transformation is directly proportional to the temperature, whilst, on the other hand, the maltose is inversely so. We are also struck with this remarkable fact, that with the exception of the transformation carried on at 66°C. (150·8°F.), the conversion of starch into dextrin and maltose, and the subsequent hydrations of the higher dextrins into the lower seem to be almost completed by the end of the first 15 minutes, and even for the transformation at 66°C. there is a fall of angle of only 10° from 15 to 60 minutes, whilst for the first 15 minutes the fall is three times as much.

TABLE VII.

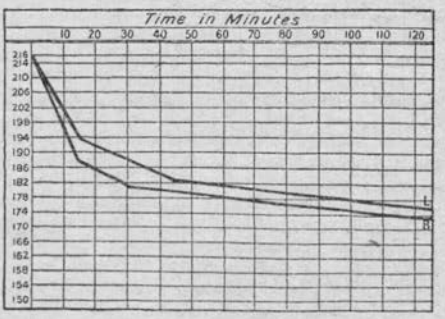


A, Transformations with unheated malt extract at 40°–50°C.; B, ditto, heated to 60°C.; C, ditto, heated to 66°C.; D, E, ditto, heated to 75°C.

On the large scale in the brewery, where the process of mashing is carried on under the normal conditions, the transformation shown at 66°C. is the one which usually takes place.

This may be seen by referring to the curves shown in Table VIII.

TABLE VIII.



These were deduced from a series of polarisations of worts from malt mashed under similar conditions—(A) in the laboratory, (B) in the brewery, water at the rate of two barrels per quarter of malt being used in both cases, and samples were taken every 15 minutes from time of finishing mashing.

On comparing these with Brown and Heron's curve for starch transformations at 66°, we are at once struck with the great similarity which

exists between them, the nature of the curves being almost exactly the same in both cases, a comparatively rapid fall occurring during the first 30 minutes, slow and regular hydration proceeding afterwards, but only to a slight extent, the difference in specific rotatory power between 30 minutes and 120 being only about 7° in each case, so that it may be taken for granted that the dextrin maltose ratio that is to obtain in the resulting wort is practically decided during the first 30 minutes. On comparing the curve at 66° in Table VII. with those at higher and lower temperatures, it would appear, curiously enough, as if this temperature for mashing were just on the boundary line as it were, a few degrees either higher or lower giving worts highly dextrinous and poor in maltose, or else the very opposite.

Seeing, then, what a very great influence a few degrees of temperature would appear to exert upon the composition of the wort, too much stress cannot be laid upon the necessity of attending carefully to the initial temperature of the mash, and there can be little doubt that the polarisation of samples of wort taken, say, at 15, 30, and 45 minutes from the time of finishing mashing, would give an intelligent brewer much valuable information as to the relative diastatic capacities of the several malts he may have to deal with, enabling him to form a pretty accurate idea as to the most suitable temperatures for future mashings, and giving him a more perfect control over the subsequent operations of sparging, pitching, attenuating, &c.

By an intelligent restriction of the diastase in the mash tun by means of careful manipulation of the initial temperatures, therefore, a brewer is able to regulate approximately the carbohydrate matter which will exist in the finished beers.

Thus for stock ales a comparatively high percentage of carbohydrates, unfermentable by primary yeast, is necessary in the beer at time of racking, consequently rather high mashing heats are employed. Using an average pale ale malt, an initial temperature of from 68° to 70°C. (155°–158°F.) is usually obtained with underlet at 77°C. (170°F.). For mild ales where a low percentage of unfermentable carbohydrates is desirable in the beer at racking, comparatively low heats are necessary, and an initial temperature of 62°–64°C. (143°–148°F.) is usually obtained with underlet at 82°C. (180°F.). In the case of black beers, where high-dried malts are used which have rather low diastatic activity, low mashing heats are essential to encourage diastatic action. An initial temperature of 61°–63°C. (142°–147°F.) is usual with underlet at 82°–87°C. (185°–190°F.), so as to raise the mash to 66°C. (152°F.) after 20 minutes' stand. Of course, the mashing temperatures vary with the quality of the malts, but the above are within the range of temperature employed. The initial temperature is determined either by inserting a thermometer specially made for the purpose into the mash in the tun, or by fixing a thermometer in the shoot leading from the outside masher into the mash tun.

During the operations of sparging, some of the harder portions of the starch which had hitherto escaped saccharification become dissolved out and transformed by the diastase still remaining into dextrin and maltose. If the sparging be applied at too high a temperature, this starch becomes gelatinised, but, in great part unconverted, owing to the destruction of the diastase at these temperatures, passes on into the wort, and although this starch of itself exercises very little if any injurious influence on the finished beer, it nevertheless serves as an index of other dangers, for the high sparging temperatures which bring into solution some of the previously unacted upon starch, also cause some of those nitrogenous bodies which at the ordinary mashing temperature are quite insoluble, to become partly soluble, especially in the presence of the saccharine matter of the wort; and these, finding their way in a state of semi-solution into the finished beer, cause a persistent cloudiness, which neither finings nor storage can remove, besides offering encouragement to the development of hurtful germs always present to a greater or less extent in freshly racked beer.

As soon as the mashing process is considered to be complete, which is generally about 2 hours after starting, the taps leading from the various underlets are opened, gently at first and afterwards more quickly, till the liquor runs half-bore and the wort is allowed to flow into the underback. The first few barrels that come over are generally cloudy, owing to the presence of small particles of the mash which have passed through the perforations in the false bottom, and partly from a reduction of temperature of the wort through coming in contact with the cold pipe. This cloudy wort is returned to the mash tun. As soon as the taps begin to run fairly bright the wort is allowed to flow from the underback into the copper.

When the mash is completed and the wort is running into the copper, the temperature of the liquor, or tap heat, as it flows from the taps is taken. This is generally done about half an hour from time of first setting taps.

30. **Sparging.** After a certain number of barrels of wort have been drawn off, a further quantity of mashing liquor is sprinkled over the goods by means of a sparger, for the purpose of washing out as completely as possible the wort still adhering to the insoluble matter or grains in the mash tun. The sparger (Fig. 10, E) consists of two or more hollow arms perforated along one side and extending to the sides of the mash tun. The older forms are connected with a central basin through which the upright shaft of the mashing machine passes, and the basin runs on wheels fixed to a carriage on the upright shaft. The mash liquor flows into the central basin, thence along the arms and through the perforation, causing the arms to revolve; by this means the whole of the goods are exposed to a washing operation, whereby the greater part of the residuary wort matter adhering to the grist is abstracted.

Great improvements have been made in spargers, with a view to increasing the extract obtained from the goods. In the latest forms the perforations along the arms are made very fine, thereby causing the liquor to issue in a fine spray, which is thoroughly and evenly distributed over the whole surface of the goods. The liquor passes through the central shaft straight into the arms, which, being hung on ball

bearings, ensure a steady revolution at any speed.

Most brewers begin sparging shortly after setting taps, and keep the sparges going continuously until the whole of the wort matter has been got away from the grains; others do not commence to sparge until one-fourth, one-half, or even three-fourths of the strong liquor has been drawn off. It is preferable to start sparging when the first ten barrels of wort are in copper, at the rate of one-half to three-quarters of a barrel per quarter of malt, at a temperature of 170°F., and until the upper layers of the mash, which have begun to cool somewhat, are again at the normal temperature; the sparging liquor is then cooled to 160°F. and the sparging carried on continuously at this temperature until the copper is made up. If higher temperatures than these are used, a risk is incurred of dissolving out some of the unaltered starch, of which there is always to be found a small portion remaining in the grains, and which has not been acted on by the diastase on the malt.

It was at one time the custom to shut off the taps when the gravity of the wort had fallen to about sp.gr. 1005, as wort below that point was thought to contain matters detrimental to the production of sound beers. In the writer's opinion this is quite a mistaken idea, and there is no reason why the wort should not be run to as low a gravity as possible. This course has been adopted in most up-to-date breweries at the present time.

31. Boiling. As soon as the wort leaves the

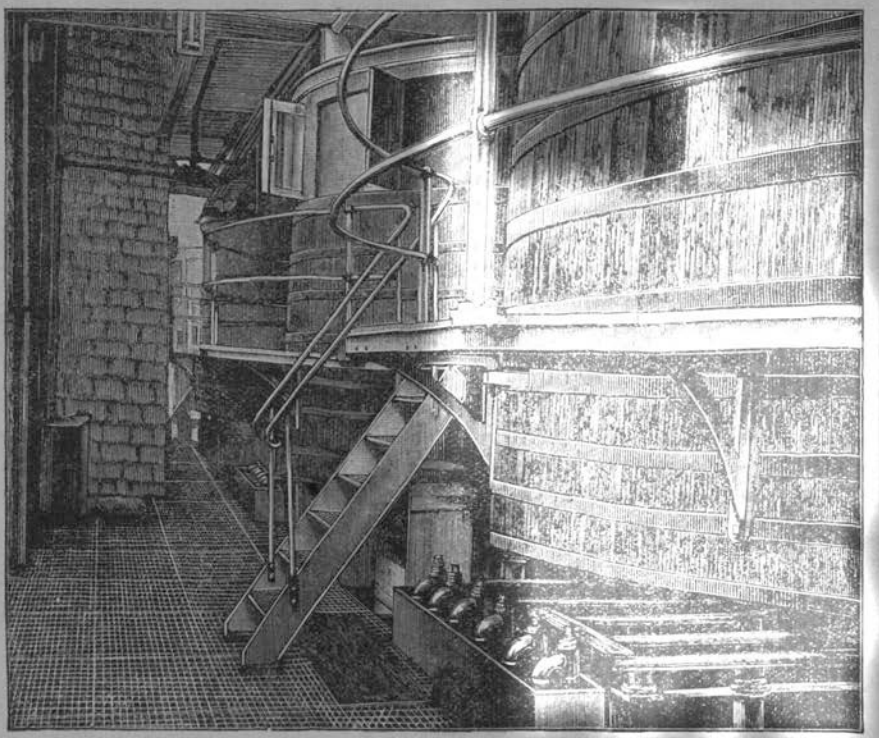


FIG. 12.—MASHING ROOM, ANGLO-BAVARIAN BREWERY, SHEPTON MALLET.

mash tun it is, as we have already seen, either run directly into the copper or collected first in an intermediate vessel called the underback, but it is advisable that it should remain only a short time in this vessel, so as to prevent any appreciable loss of heat. As soon as the first ten barrels are in the copper the fire may be got up, and the temperature of the wort raised to about 180°F. or 190°F. At the same time, a certain proportion of the hops may be added a little at a time until all the wort is run into the copper or the copper is made up. As soon as this is effected the fire is increased and the wort brought to the boiling-point as quickly as possible. This is carried on usually for one and a half to two hours.

In some breweries it is the custom to keep the wort as it flows into the copper at a temperature not exceeding 165° during the time the copper is being filled. This process is called stewing the worts, and is said to be often very advantageous, especially when the malts are deficient in diastatic power. No advantage can possibly accrue from such a process, but, on the contrary, much harm may result therefrom to the finished beer. With regard to the period at which it is most advisable to add the hops, much difference of opinion exists, some brewers not adding any until the copper is nearly or entirely made up, others adding the whole of the hops before the copper is half full. Both methods are very objectionable; the addition of the hops to the copper ought to run *pari passu* with the inflowing wort. By this means we get a more

regular precipitation and coagulation of certain albuminous substances from the wort, and a more even extraction of the bitter and resinous principles of the hop, the result being a well-broken, regular wort and superior-flavoured beer. The usual plan in many breweries, and one which for several reasons is to be strongly recommended, is to divide the total quantity of hops for each copper into three portions. The first portion is added as the wort is running in, a relative proportion for every 10 barrels of wort as it runs into the copper until made up; the second portion is added after one hour's boiling, and the third portion half an hour before the copper is turned out.

It is the general custom to use a blend of several varieties and qualities of hops, and in this case the most inferior are added in the first portion, the second portion consists of superior hops to the first, and the last portion are choice hops selected to impart to the beer its special character. By this method most of the volatile oils and resins of the last portion of hops will remain in the beer, imparting to it a characteristic delicate aroma of flavour.

We have assumed that the whole of the wort from one brewing is boiled at once in one copper, and, where practicable, this is by far the best plan; but more often the wort from one brewing is divided between two coppers, the stronger wort being boiled in the first copper with the whole or greater part of the hops, whilst the last half and weaker portion of the worts is run into the second copper and boiled with the already exhausted hops which are returned from the first copper. This is a very objectionable as well as dangerous method of procedure. The first copper wort will contain proportionately much more saccharine than nitrogenous matter, the latter being in excess in the second copper; again, all the tannin and the largest proportion of the soluble matters are extracted from the hops by boiling them in the first copper, so that when these hops, which are practically exhausted of all their useful properties, are added to the second copper of wort containing relatively more albuminous matter than the first, comparatively little precipitation or coagulation is produced by the matter extracted from the hops, whilst a coarse, bitter flavour is imparted to the wort, so that the resulting beer contains an excess of nitrogenous matter, thereby being rendered more liable to disease, and brightening only with difficulty. Where it is necessary to divide the wort between two coppers, the stronger wort may be run into one and the weaker into the other, but to both coppers fresh hops should be added in quantities proportionate to the gravities of the respective worts.

During the boiling of the wort with hops in the copper, all diastatic action is completely destroyed, and the starch products become fixed, a large proportion of the hitherto soluble albuminoids are precipitated, whilst a small quantity of hop extract is added; at the same time, a slight alteration occurs in the carbohydrates other than those derived from the starch, being probably due to a slight inversion of a part of the unacted-on cane sugar by the acid of the boiling wort, but practically, the actual composition of the starch products is unaltered during the boiling process, so that the wort at this stage affords a very good index as to the dextrin percentage of the resulting beer, and hence a systematic polarimetric examination of wort from the copper will be found to be extremely useful. It may be taken as a general rule that the specific rotatory power of a wort should not fall below 105° $[\alpha]_D$ or rise higher than 122° $[\alpha]_D$, the former indicating an abnormally low percentage of dextrin and large excess of soluble nitrogenous matters, the latter a very high percentage of dextrin resulting probably in extremely high attenuations and cloudy beers, fining only with difficulty.

When the boiling process is completed, the wort with the hops is run out of the copper into the hopback. This is a vessel of somewhat similar construction to the mash tun; the sides may be square or circular in shape, preferably the latter, and is furnished with a perforated copper false bottom. Here the wort is drained from the hops and run into a small wooden underback, whence it is pumped up on to the coolers, but as the hops in the hopback retain a certain proportion of the wort adhering to their surface, boiling water is sparged over them, and these spargings are added to the wort and serve to reduce it to the required gravity. Where brewing sugar of any description, whether cane sugar, invert, or glucose, is used in the brewing, it is best to add the requisite quantity previously dissolved in boiling water to the wort in copper about 15 minutes before turning out; the usual proportions are from one-third to one-fifth of the quantity of malt used, 2 cwts. of sugar being reckoned to be equivalent to the extract yielded by 1 quarter of malt. The quantity of hops used will, of course, vary with the gravity as well as quality of the wort. In Burton as much as 20 lbs. of hops per quarter of malt have been used for export pale ales, but for ordinary pale ales from 10 lbs. to 15 lbs. is the usual proportion, less being required where malt substitutes such as invert sugar or glucose are used.

The main effects of boiling the wort with hops in the copper are: evaporation; sterilisation, *i.e.* destruction by heat of all bacteria and disease organisms obtained from the malt and from the air; destruction of all diastatic and proteolytic action, and fixation of the starch products; precipitation of a large proportion of the hitherto soluble albuminoids; and the addition of hop extract consisting of the bitter principles and tannin.

Two systems are in general use, viz. boiling by fire and boiling by steam. It is essential that the stability of a beer should be fixed by a thorough cooking of the wort, and this is readily achieved in a suitably deep fire-heated copper, but it is rather doubtful whether the same result is obtained in a copper heated by steam.

In the case of a fire copper, we have on one side of the plates intense heat and on the other side cool wort. The circulation of the wort is excellent and a vigorous boil results. There is also a continuous exposure of a layer of wort to a very high temperature on the bottom of the copper, which receives the thorough cooking which is so essential. In the case of steam coppers, the contact temperature is very much lower, for although a tumultuous boil is secured

by the aid of coils and heaters of various design, the temperature obtained is high and the evaporation rapid. Still the wort does not receive the same 'cooking' that it does in a fire copper and upon which the final stability of the beers so much depends.

32. **Cooling.** Coolers may be described as large shallow tanks about 18 inches deep, of such capacity as to contain the whole contents of the copper at one time; they are generally constructed of wood, wood lined with sheet copper or iron. Those made of wood are rapidly being discarded, as they are so liable to retain contamination in the way of spores of bacteria or mould.

The principal object in running the wort on to the coolers is undoubtedly to lower the temperature or to take the 'fire heat' out of it; but at the same time, another action is going on, the importance of which has only been clearly understood during the last few years, and that is the aëration of the wort or the absorption by the wort of the oxygen of the air, either by way of solution or of combination, for not only does the atmospheric oxygen become dissolved in the wort in a manner similar to carbonic acid in water, but it actually enters into direct chemical combination with certain nitrogenous constituents of the wort, rendering them thereby insoluble and causing such substances to be deposited on the coolers. Aëration has also a considerable influence on fermentation, indeed, 'in the ordinary process of brewing normal fermentation would be almost impossible, and in every case most defective, if the wort, before being run into the fermenting vessels were not aërated by its passage over the coolers, where the aëration is more or less effective according to the depth of liquid on the coolers.' It is evident, then, that it is decidedly advantageous to allow the wort to remain a certain time on coolers before passing it on to the fermenting rounds, and also that the surface liquid should be drawn off first. This has been effected in a very ingenious manner by the arrangement shown in Fig. 13, which is the invention of Mr. S. Briggs, of Burton-on-Trent.

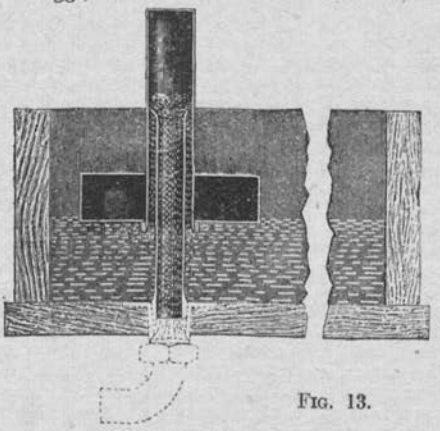


FIG. 13.

This apparatus simply consists of a vertical tube made of metal, fixed over the outlet of the cooler or vessel.

When the wort or other liquid is ready to be run off, the tube is filled with liquor, the float placed over the tube, and the outlet tap opened; the wort or liquid at once begins to run over the top of the tube and continues doing so until the whole is run off from the cooler or vessel.

The supply of liquor always being taken from the top, the brightest and coolest wort is run down first, so that the whole or greater part of the sediment is left on the cooler.

It likewise gets a bright wort down over the refrigerator into the fermenting tuns, for while the bright wort is running off from the top, the grounds and thick sediment sink to the bottom, and remain on the coolers.

The wort is usually delivered on to the cooler through a perforated pipe in the form of a spray for the purpose of aëration, and during the summer months in some breweries in order to prevent bacterial contamination on the coolers, these are replaced by deep tanks, the spraying of the wort being found sufficient to absorb the necessary oxygen, the whole of the cooling in this case being effected over the refrigerators.

After leaving the coolers, the wort, which is not yet by any means cold, is passed over a refrigerator, where it takes up in its passage a still further quantity of oxygen. There are several forms of refrigerators; the vertical one such as shown in Fig. 14 is generally considered the best.

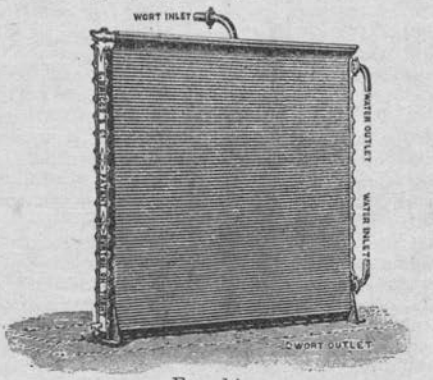


FIG. 14.

These refrigerators are made from seamless copper tubes, with a rib or feather on bottom and groove or channel on top side, running full length of tube. The rib or feather of one tube is securely fastened into the groove or channel of the next tube, thus giving great solidity, and presenting an even surface to prevent any liability of dirt accumulating, the brewer being able at a glance to see if the machine is perfectly clean.

The ends are fitted with gun-metal boxes with movable caps, giving easy access for brushing out the tubes, and are especially adapted for pumping, the tubes having no divisions to impede the water passage.

They are fitted with adjustable feet for regulating the flow of wort, and a perfect capillary attraction is obtained, a great desideratum in vertical refrigerators. The inlet trough is divided to secure an equal flow of wort down both sides of the machine.

But all the time that the wort is on the coolers and refrigerator it is exposed to danger

of contamination with germs of disease such as bacteria and wild types of yeast, which are to be found always floating about in the air. Also beyond a certain limit aëration is injurious to the palate characteristics and aroma of the finished beer, hence it is advisable that, consistently with sufficient aëration, the wort should be cooled as quickly as possible, especially when it reaches a temperature of 170° and lower. Coolers and refrigerators should therefore be of sufficient capacity to cool the whole of one brewing or gyle down to the required temperature, 58°–60°F., in at least six hours, counting from the time the first of the wort is pumped on to the coolers until the last of it is in the fermenting vessel. This temperature will vary slightly with the quality of the wort and the temperature of the atmosphere; but for beer of medium strength, and where the atmospheric temperature is about the average, 58°–60°F. in winter and 58°F. in summer may be taken as safe temperatures for cooling the wort to, previous to adding the yeast.

It has long been recognised that most of the disease organisms that find their way into the beer are introduced by the air, and as soon as the wort on the coolers and refrigerators drops below 170°F., wild yeasts and acid-forming bacteria are no longer killed. It is advisable, therefore, unless the air playing on the wort is sterilised, that the temperature should not drop lower than 170° while the wort is on the coolers. In the case of the refrigerators, however, the conditions are different. Here aëration is essential as well as the cooling of the wort to temperatures favourable to the growth of disease germs. There is an extended film of liquid in contact with the air, and the organisms in the air coming in contact with the film are attracted by it, and, being of a viscous nature, the wort retains a large number of them. It seems very essential, therefore, to conduct the process of refrigeration in a sterile atmosphere. This idea, in fact, is being adopted in a great number of breweries at the present time. The

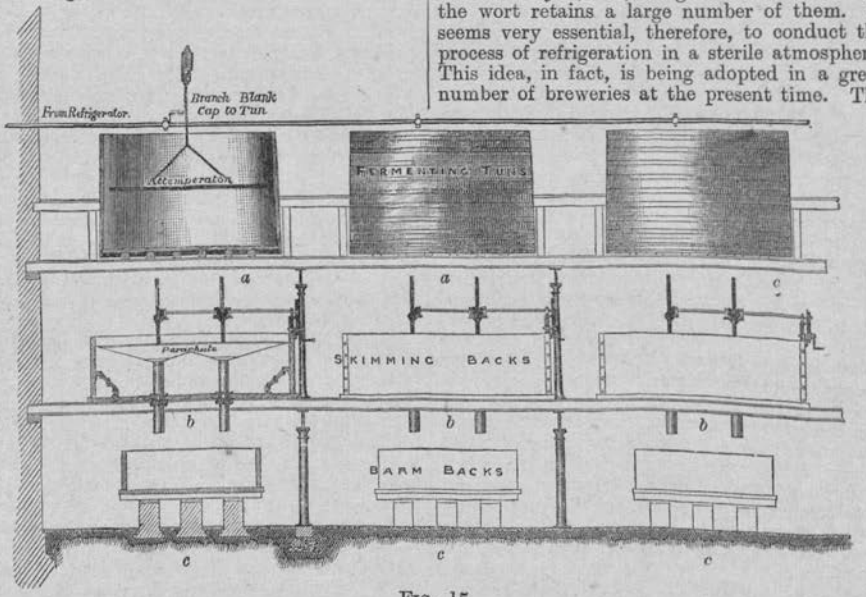


FIG. 15.

refrigerators are enclosed in an air-tight room, the walls and ceiling of which are made of material which is easily cleansed and which is supplied with an inlet and outlet for the sterile air. During the time the wort is running down, previously purified air is blown through the room at a sufficient rate to renew the atmosphere at least twenty times in order to ensure efficient aëration and also to remove the reek.

There are several air purifiers in use at the present time, but the principle is the same in all cases, and consists in blowing air by means of a fan over an adhesive or viscous liquid containing a germicide. This liquid absorbs all the micro-organisms from the air, which issues from the outlet in a perfectly sterile condition.

Of course, it is essential that the ceiling, walls, and floor of the refrigerator room should be perfectly clean, as it would be useless to inject pure air into a room in an unclean condition.

33. **Fermenting.** From the refrigerator the wort is conveyed by copper pipes to the fermenting tun (Fig. 15, *a*). This is usually constructed of wood, and may be square or round, preferably the latter, as being more easily cleansed. The wood generally preferred is Dantzic deal, but care must be taken before using vessels made with this wood to first remove its resinous flavour from it before running in the wort. The surfaces of wooden vessels should present a perfectly smooth interior surface, otherwise they become very readily contaminated. On this account, copper in thin sheets has been very extensively employed for lining these vessels. This is undoubtedly the finest material that can be employed, as it is so very readily cleansed, is not liable to contamination, and is extremely durable. The fermenting round is furnished with an attemperator or coil of pipe through which either hot or cold water may be transmitted for the purpose of regulating the temperature of the fermenting wort. As soon as the first ten barrels of wort are in the fermenting tun the requisite quantity

of yeast may be added; this is called 'pitching.' The quantity of yeast to be added will of course vary according to the strength of the wort, the quantity of hops used, quality of yeast, and season. For light ales and running beers about ¾ lb. to 1½ lbs. per barrel of wort are used, whilst for the stronger ales from 1½ to 3 or even 4 lbs. in some cases are used.

In general appearance the yeast should be of a rich cream colour, possessing a sweet clean smell. Under the microscope the cells should be uniform in size, full and plump-looking, and transparent, containing few, if any, vacuoles or granulations; the cell walls should be thick and free from pittings, and stand well out against the field. No signs of budding should be apparent, and no dead or shrivelled cells should be present. The presence of any dead cells may easily be determined by running on to the slide a drop of methylene-blue solution, which *instantly stains all dead matter, but has no effect on living cells.* In a really good pitching yeast no bacteria or other germs of disease ought to be present, but most yeasts generally contain a few. As a rule, any sample of yeast that contains more than 20 short bacteria (rods) in 10 fields ought to be condemned for pitching purposes; the presence of any of the longer forms of bacteria, whether straight or bent, is sufficient to at once condemn the yeast as being a highly dangerous one to use.

As has already been mentioned, it is almost impossible to determine by ordinary microscopical examination the presence or absence of wild types of yeast; these must be looked for by Hansen's method of ascospore formation.

As soon as the wort has been cooled to the proper temperature, and ready to undergo the process of fermentation, it is, according to the Inland Revenue Act of 1880, run into a vessel called the collecting vessel, where it must remain for a period not less than 12 hours, or until such time as the Excise officer can determine its gravity and bulk for the purpose of levying the required duty. In most breweries these collecting vessels are the fermenting tuns themselves.

After all the wort has been run into the tun and the yeast thoroughly roused up with it, the process of fermentation commences; bubbles of gas rise to the surface until, after a while, the whole of the surface becomes covered with a creamy froth. As the fermentation progresses and the decomposition of the sugar becomes more rapid, the greater is the amount of carbonic acid which is liberated, and the froth swells up to such an extent that at last, not being able to resist any further tension, it topples over, giving rise to that 'rocky' appearance which is seen on the surface of healthy fermentations during the earlier stages. At the same time, the temperature of the liquid will be noticed to rise steadily. If this goes on too fast it must be checked to a slight extent by running some cold water through the attemperator. Under normal conditions a rise of 1° ought to take place in 6 hours, so that at the end of about 60 hours the temperature of the fermenting wort would have risen to 70°F.; the beer will at the same time have attenuated to about one-half. Thus a beer wort which had a specific gravity of 1050 at time of pitching will now show an apparent specific gravity or attenuation of about 1023.

This is about the highest point the temperature is allowed to rise to. When, therefore, this point is reached, the separation of the yeast from the beer, or the cleansing process, is commenced.

Up to this stage from the time of pitching, the fermentation is very closely watched by the brewer, and the temperature and attenuation taken at intervals of about five hours. If the fermentation goes on too rapidly, it is easily controlled by running more water through the attemperator.

When the yeast is first added to the wort it lays hold of the free oxygen which has been dissolved by the passage of such wort over the refrigerators, and not until the greater portion of that oxygen is used up do the yeast cells begin to attack the sugars of the wort and split them up into carbonic acid and alcohol. It has been found in practice that the fermentation proceeds more satisfactorily if a certain amount of aëration is carried on during the process. This can be done by pumping air into the tun of fermenting wort, but yeast not only requires a limited amount of air, but also a vigorous motion from time to time, in order to enable it to do its work effectually as well as to render it capable of being eliminated from the beer. Hence a thorough rousing by means of long paddles or oars worked with hand, or by some form of the various machines introduced for this purpose, is necessary at stated intervals, more especially where the fermentation is inclined to be at all sluggish.

During late years, owing to the general use of malt and substitutes devoid of yeast nutriment in brewing, the more highly dried character of the malt in use, defects of much modern malt attributable to variation and inferiority of barleys wetted, and reduction in gravities of collected worts, several forms of nutriment for the yeast have been introduced. These consist chiefly of peptones and amides which have been proved to be the best nitrogenous nutrients of yeast.

34. **Cleansing.** The separation of the yeast from the beer may be accomplished in many ways. The three principal systems are known as:

The *cleansing system*, as practised in some London breweries, and also in Burton, but on a very much improved method.

The *skimming system*, as generally adopted throughout the South and West, as well as many other parts of England; and

The *stone square system*, which is almost exclusively confined to Yorkshire.

In London, and indeed in many country breweries, the cleansing is effected by running the beer from the fermenting tun by means of a hose into ordinary 36-gallon casks, arranged in rows side by side on a wooden trough or stillion, about 2 feet from the ground. The beer remains in these casks for some days, the bunghole being left open, and through it the yeast works out and falls into the stillion. As the yeast works over, more beer is added to each cask, so that by the time the beer is freed entirely from the yeast, each cask is full and ready to be bunged up, and sent away for consumption, for London beer fermented upon this

system is generally drunk within a week. This method of cleansing is, however, being rapidly replaced by the skimming system; this in principle simply consists in skimming off the yeast from the surface of the liquid from time to time as it rises to the top, and may be effected either in the fermenting tun itself, or, which is much preferable, in the cleanser. The beer, when it has attained the proper degree of attenuation and temperature, is run down from the fermenting tun along with the yeast into a large square wooden tank called the skimming back or settler (Fig. 15, *b*). This is fitted with attemperators which run round the sides; at one end are fixed two parachutes, which are simply large flat funnels of copper having pipes 4 inches in diameter attached to them, the whole being tinned over, and capable of being raised or lowered at pleasure by means of a screw and winch handle.

When the liquor is run into the settler, owing to the thorough aëration which it receives in so doing, a vigorous fermentation takes place, and unless carefully watched the temperature

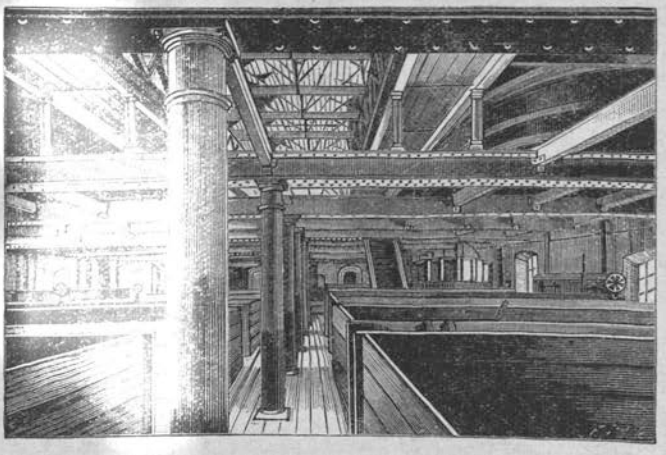


FIG. 16.—TUN ROOM AT ANGLO-BAVARIAN BREWERY, SHEPTON MALLET.

is apt to rise. At this point attemperation must be attended to, but the fermentation must not receive too severe a check. Soon a film of yeast mixed with carbonic acid gas appears on the surface of the liquid, which gradually gets thicker, so that about 6 hours after tunning or running into the cleansing tank, the first head of yeast is ready to be skimmed off. This is done by means of a plank as long as the tank is wide, furnished with handles, and held vertically by two men at the end opposite to the parachutes, in such a position that one end of the plank just touches the surface of the liquid immediately beneath the head of the yeast. This plank is then gradually moved along the length of the tank, pushing the yeast before it. The parachutes are fixed so that they will just receive the yeast which overflows into them, which is then conveyed into slate tanks placed immediately beneath (*see* Fig. 15, *c*). Here it is allowed to remain for some hours, being roused occasionally so as to drive off the carbonic acid gas as well as to enable the beer which has come over with it to settle out, and which is drawn off through a tap at the bottom of the tank. The yeast is either pressed and sent away, or used for pitching fresh wort.

After the first skimming, the yeast still continues to throw up a cleaner and whiter-looking head, so that in about 3 or 4 hours' time a second skimming is made, and so on every 3 or 4 hours until all of the yeast has separated from the beer. It is generally found that from four to five skimmings are necessary to effect this. After the last skimming a thin but tough film of yeast forms on the surface; this is allowed to remain, and serves as a covering to protect the beer from aërial contamination and from oxidation, as well as to prevent the escape of carbonic acid. A general view of these skimming backs is shown in Fig. 16.

It usually remains from two to three days in the settlers after the last skimming, so as to allow all matters in suspension to settle out. At the end of that time the beer, which is now very nearly if not quite bright, is run down into a large tank, termed a racking square, where, after remaining a few hours, it is racked off into trade casks, either to be sent away for consumption or to be stored for some time to mature.

The Burton Union system, as the Burton system of cleansing is called, may be regarded as the scientific development of the old London system of cask cleansing on stillions. In this system a number of casks or unions (Fig. 17) capable of holding four barrels of beer, are placed side by side in two rows; these are hung in sets of twelve or more on a substantial frame, so as to admit of a free revolution of each cask on its axis, so that when the casks are to be washed they can be filled with boiling water, bunged up, and rapidly revolved. Supported on the same frame, and immediately above and running parallel with these rows of casks, is a long shallow trough called the yeast trough, and at one end and at right angles to it is another trough called the

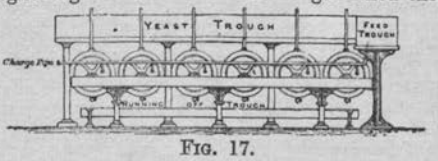


FIG. 17.

feeding trough. From this trough a pipe, 2 inches in diameter, runs along the whole length of the series of casks on either side, and is connected with each cask by T-pieces and screw unions. At the highest part of each cask is fixed a ground-brass socket, into which is fitted a peculiarly shaped pipe of tinned copper, termed a swan-neck, which is arranged to bend over the yeast trough, and serves to convey the yeast thrown off during cleansing to

this trough. In order to keep the casks full a certain quantity of wort is placed in the feeding trough, which is allowed to run into the casks from time to time to replace the yeast (and beer carried over with the yeast) which has worked over into the yeast trough. After a time the beer carried over with the yeast separates out and is allowed to flow into the feeding trough through a series of holes in the end of the yeast trough nearest to the feeding trough, of which it forms one of the sides; these holes are closed with corks, and the man in charge ascertains by trial at which holes the beer will run off free from yeast, and accordingly opens these in turn so that the casks are always kept more or less full of beer. This feeding or sparging is done at intervals of 3 hours until the active fermentation has ceased. After the fermentation has subsided, and no more yeast is observed to come over, the swan-necks are removed, the casks bunged up, and the contents allowed to remain at rest for a few days longer for the purpose of allowing any yeast or other matters that may have remained in suspension to settle down to the bottoms of the casks. The clear ale is then drawn off by means of a screw tap fixed at the lower part of each cask. The tap projects 6 inches upward into the cask, so as to prevent the sediment or grounds from being drawn off at the same time as the clear liquor. From these taps the finished beer is delivered by means of a trough running underneath them into a large settling back or racking vessel, where it is allowed to settle for a short time before being drawn or racked off into trade casks.

Where the Union system is employed, no attemperators whatever are used in the fermenting tuns, the time for the beer to be tunned being regulated entirely by the temperature. As soon as 70° is attained, the beer is immediately run into the unions. Neither are any attemperators used in these casks in winter, but during the summer months free recourse is had to attemperating. Fig. 18 gives a very good idea of the Union system of cleansing.

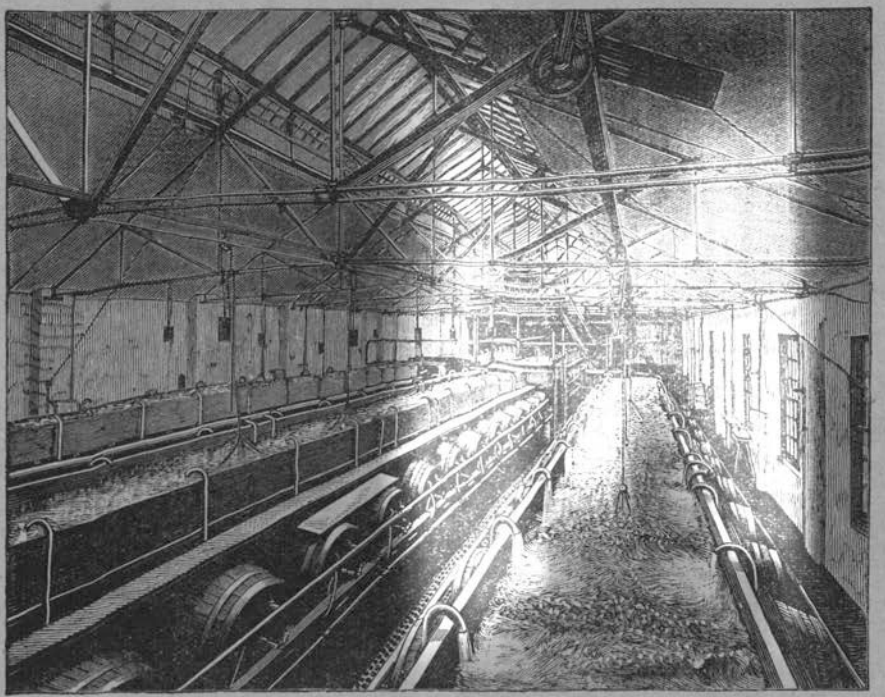


FIG. 18.—UNION ROOM AT MESSRS. WORTHINGTON & CO.'S BREWERY, BURTON-ON-TRENT.

Where the Stone Square system is used, the squares are constructed of stone or slate, and have a capacity of about 30 to 50 barrels. The vessels consist of two parts: the lower one, which has double sides and a space between for attemperating liquor; and the upper one, which is placed so that its bottom forms a top or cover to the one below. In this roof or cover, there is a man-hole with a raised collar about 6 inches high and also a smaller hole provided with a valve, on the under side of which a tube, called the organ pipe, is connected, which extends to within a few inches of the bottom of the square. The lower vessel is a little more than filled so that the wort lies some 2 or 3 inches deep in the upper one or yeast-back. About 36 hours after pitching, pumping is started and carried on at regular intervals until attenuation is nearly over, wort being pumped into the top-back, well roused and mixed with the yeast that has risen there, and allowed to flow back into the lower vessel through the 'organ pipe.' The whole crop of yeast is eventually left in the upper back.

This system is productive of an excellent yeast crop and bright racking beers and of very brisk, well-conditioned beers with good palate fulness. Owing to the trouble of effectually

cleansing these vessels, and several other difficulties met with, they are gradually going out of use.

Space will not permit us to enter into a detailed description of the various other systems of fermentation carried on in this country, and we must now pass on to treat very briefly of the German system of beer-brewing.

The German or decoction method of mashing is generally carried out as follows:—

Ground malt is run into the mash tun, in which are two-thirds of the required water at the ordinary temperature of the air; here it remains for 2 hours. In the mean time the remainder of the water is heated to boiling in the copper, and then run slowly into the mash tun, the rakes at the same time kept revolving at a good speed. By this means the temperature of the mash is raised to 95°–100°F. The first thick mash (about one-third of the whole) is now drawn off into the copper and boiled for 30 minutes, and then returned to the mash tun, the temperature of which is thus raised to 116°F., the rakes being kept going during the addition of the first boiled mash. A second thick mash is now drawn off into the copper and heated to boiling-point, and kept boiling for 15 minutes, and then run back again to the mash tun, the temperature being now raised to 149°F. After this the clear part of the mash is run off and boiled in the copper for 15 minutes and run back again to the mash tun; the temperature of the mash is now 167°F. The mash is now covered up, and allowed to lie for one to one and a half hours; the taps are then set, and the clear wort boiled for 2 hours with hops at the rate of about 2½ lbs. of hops to every 100 lbs. of malt used. The wort is then drawn off and run over coolers and refrigerator, where it is cooled down to 40°F., and thence to fermenting tuns, which are generally placed under ground in order that they may be kept cool by ice; and for that purpose small fermenting vessels of about twenty barrels' capacity are used. These are filled nearly full with the wort, and bottom yeast in the proportion of about 1 lb. to every five barrels of wort added; the yeast, previous to being added to the wort, is first mixed with some wort of the former day's brewing, and thoroughly aërated by repeated pouring from one vessel to the other, and then put aside in a warm place for some hours, so that by the time the wort is ready to be pitched a lot of new and vigorous yeast cells have already formed and the fermentation is well started. During the earlier stages of fermentation a slight head rises to the surface; later on the yeast deposits on the bottom of the fermenting vessels. During this primary fermentation, which lasts about 12 days or more, the temperature of the fermenting wort is kept at about 44°F. When the primary fermentation is finished, the attenuation has run down to about one-half the original gravity of the wort, and the beer is run off, as free as possible from sediment, into casks, ranged in tiers on either side of large cellars, which are kept cold by ice. Here they are allowed to remain for some months, during which time a secondary fermentation goes slowly on, and the beer gradually clears itself until it becomes brilliant and fit for use.

Where beer is required for quick consumption it is usual, in order to enable it to become bright rapidly, to add a solution of isinglass, or 'finings' at the rate of 1 to 4 pints per barrel of beer.

The isinglass unites chemically with the tannic acid which is nearly always present in beer, forming a gelatinous flocculent precipitate of tannate of gelatin; this very soon sinks to the bottom of the cask, carrying all matter in suspension with it, and leaving the beer clear and brilliant.

Finings are generally made by dissolving isinglass in sour beer. This is a crude and dangerous method. In the first place, the isinglass takes several weeks to dissolve, and secondly, by means of this sour or turned beer a great risk is run of introducing into the sound fresh beer all kinds of disease germs, but more particularly *S. pastorianus*, as well as the ropy and lactic ferments.

The best and purest finings are undoubtedly made by dissolving good isinglass in dilute solution of sulphurous acid, and on no account should any other kind of finings be used in the brewery.

Beer which is not required for immediate use is stored in cellars at a temperature of 54°F., either in vats or in the casks in which it is to be sent out. Such beers are generally not fined, and each cask is furnished with a porous spile or vent peg to allow of the escape of a portion of the carbonic acid produced, owing to a secondary fermentation which always sets up in casks when beers are stored for any time.

Chemical analysis of a beer should be made shortly after racking, and before the secondary fermentation in cask has commenced. Such an analysis, calculated on the solid extract of the original unfermented wort, should show:

a. Matter fermented.
b. Maltose unfermented.
c. Dextrin unfermented.
d. Albuminoids, ash, &c.

As the character and keeping properties of a beer depend to a very large extent on the percentage of unfermented dextrin which it contains, it would appear very desirable that an analysis of those beers required for stock or export should occasionally be made, so that an idea may be obtained as to the constancy or otherwise of their composition, and hence their suitability for the purpose for which they were intended.

Generally, at time of racking, and indeed in some cases at different stages of the brewing process, some form or other of antiseptic is added to the beer for the purpose of protecting it against the germs of disease to which from one cause or another it is so subject. The substances most generally employed for this purpose are calcium bisulphite, salicylic acid, or a particular form of potassium sulphite, known as kalium metasulphite. The antiseptic, whatever it may be, is added either to the beer whilst in the racking square, or to the beer in cask just after racking, if calcium bisulphite at the rate of ¼ to ½ pint per barrel, or salicylic at the rate of ¼ oz. or less per barrel.

Experience shows that calcium bisulphite is much to be preferred to salicylic acid, but the chief objection appears to be the smell which it sometimes imparts to the beer, especially when

used in any quantity. This may be got over by using kalium metasulphite, which is claimed by the discoverers to be much more powerful in its action than bisulphite, whilst it imparts no smell to the finished beer.

Absolute cleanliness in every part of the brewery and in every portion of the plant is necessary, for unless due regard be paid to this point, no matter how good the materials or how perfect the process of manufacture, the quality of the finished article will be sadly defective in its most vital characteristic, viz. keeping properties; false ferments and micro-organisms of all kinds will be taken up by the beer at all stages of its manufacture, rendering it after a time sour, unpalatable, and unfit for consumption. In order to obviate this, every portion of the plant, when not in use, should be thoroughly well cleansed and disinfected with suitable agents, such as chloride of lime, calcium bisulphite, caustic potash, &c. *Cf.* A. Hartley, Trans. of the Laboratory Club, 1, 42.

Bottled Beers.

The adoption of lower gravities by the brewer, owing to increased expenses and the rapid advance into popular favour of light bitter beers, has led to the almost general production of a beer of light gravity, distinctly though not strongly hopped, which will fine quickly and carry a good condition within a very short time of racking. The desire for good condition as well as for a convenient package has gradually created a large demand for bottled beer, and the bottling trade has now become an integral part of almost every brewery.

The various methods of bottling at present carried out in this country are as follows:—

1. Natural method of bottling.
2. Forced bottling.
3. Simple carbonation.
4. Quick chilling and filtering process.
5. Prolonged chilling and filtering process.

1. The old-fashioned or natural method of bottling can only be successfully carried out if the beers to be bottled have been specially brewed for the purpose. There are many other influences besides the materials used, such as the conditions of plant, aëration, yeast, &c., which have their action upon the flavour, quality, and type of the beers; and it will be necessary for the brewer to regulate these matters before he is able to produce a satisfactory article. The water used for mashing should be suitably hardened by the addition of gypsum and alkaline chlorides—the gypsum conducing to bright and more stable worts, whilst at the same time preventing the extraction of an excessive amount of bitter principles from the hops, and the alkaline chlorides contributing to palate fulness.

Great care must be exercised in the selection of materials, and only the best malt prepared from those barleys which are free from an excess of nitrogenous constituents should be used. A blend of good English and foreign malt with a proportion of some prepared grain will give the best results. It is also advisable to use a good quality hop with a proportion of foreign hops, on account of their greater preservative power, and only the choicest English should be used for dry hopping. It is necessary that all secondary fermentation changes should be allowed to complete themselves, and that the beer should be saturated with carbonic acid gas before bottling, so it is racked into casks and stored in a cellar at a temperature of 50°–55°F. When it is conditioned, it is fined if necessary, and bottled by means of a siphon machine into perfectly dry clean bottles, and immediately corked. The necessary bottle condition is then brought about by storing at a temperature of about 65°F. for some time before consumption.

2. When a brewer cannot afford to let his bottled beers lie for so long a period as is necessary in the old-fashioned system, he generally has recourse to the second method, called 'forced bottling.' The same type of beer is brewed as in the previous method, and the same care exercised in the choice of materials, &c.; but early fermentation is encouraged in cask, and the time of storage greatly curtailed. This is accomplished by adding priming to the beer at the time of racking, while early clarification is brought about by the addition of finings. When the beer is absolutely brilliant and has been sufficiently flattened in cask, it is bottled and stored at a temperature of 60°–70°F. It is sent out immediately it is sufficiently conditioned, and, provided it is not kept too long, it will turn out quite satisfactorily.

Naturally conditioned beers, brewed and bottled under the most favourable conditions, present to the palate a peculiar pungent flavour and an invigorating freshness which cannot easily be obtained with carbonated beer. There is one great drawback, however, to all such beers, they must inevitably be accompanied by a deposit which in many cases is more or less heavy. It was to obviate this defect that the carbonating system was first introduced, and the many and various improvements which have been made since its first introduction have made it possible to produce a beer in many respects equal to that produced by the natural method.

3. To produce a first-class carbonated beer, the same amount of care in selection of materials is hardly necessary, very high-class malts not being absolutely essential, and a certain proportion of invert sugar being a desirable constituent. The beer, however, must be specially brewed for this purpose, as it is absolutely necessary that the finished beer should possess as little fermentable matter as possible, and a very low attenuation. After racking, the beers should be fined and remain in the cellar for three weeks. It is then efficiently filtered through a pulp filter, from which it passes into an automatic carbonating machine, where it is thoroughly impregnated with gas at a pressure of 30–40 lbs., and at the same time prevented from coming in contact with any air. The whole secret of good carbonation lies in properly impregnating the beer with gas. The gas used should be pure, the natural gas, collected from fermenting wort, being preferred by some brewers, as it is said to give better results and impart a better flavour to the beer. The beer passes from the carbonator to a suitable bottling machine which fills into bottles and stoppers without waste or loss of gas. This beer can be sent out as soon as bottled, but can also be kept without throwing a deposit for some time. The greatest defect attaching to carbonated beers is that their brilliancy is influenced by the temperature at which they are

stored, as they are inclined to develop haziness in very hot or cold weather. This has been overcome by chilling the beer before filtering and bottling.

It is necessary to recognise that the usual system of brewing and fermenting must be modified to meet the altered conditions involved for producing chilled and filtered beers, and the remarks made above with regard to the low attenuations necessary for carbonated beer applies equally well for this type of beer.

By the process of chilling beer or the cooling of it down to 30°F. the yeast and other organisms, with certain of the hop resins and substances of a proteid nature which become insoluble at low temperature are coagulated and thrown out of solution. When these matters are separated at the same low temperature by filtration, the beer is rendered insensitive to changes of temperature, and freed, or practically freed, from fermentative organisms, and will therefore remain brilliant for a very considerable period.

4. The quick-chilling process consists in rapidly cooling the beer down to 30°F., thoroughly impregnating with carbonic acid gas, filtering at the low temperature, and bottling. The complete plant consists of a refrigerating machine to cool a sufficient quantity of brine to about 20°F., brine-circulating pump, one or more beer-cooling cylinders, beer filter, and bottle-filling machine. The refrigerating machines in general use are either the ammonia-compression or the carbonic acid-compression system. The cooling cylinders are horizontal cylindrical vessels, either surrounded by an outer jacket or shell around which refrigerated brine is caused to circulate, or fitted inside with a coil of pipe through which the cold brine passes, the coil being mounted on a shaft which allows it to revolve.

The beer is usually matured over hops in cask for about two weeks. The cask of beer is then transferred into one of the cylinders, which is at once subjected to the influence of cold by the passage of cold brine, and at the same time the beer is charged with carbonic acid gas. The temperature of the beer is quickly brought down to 30°F., when it is allowed to rest a short time. It is then filtered through an efficient pulp filter and bottled by means of a bottling machine.

The beers produced by this method leave very much to be desired both as regards flavour and palatefulness, but the process has found favour with many brewers, as it is very easy to manage and requires no storage or lengthening maturation.

5. The balance of opinion, however, is in favour of the slow as against the quick-chilling system, for undoubtedly the nearest approach to a well-matured beer is one which by natural generation of its own carbonic acid gas in cask or other vessel is afterwards allowed to cool down slowly, and thus redissolve the free carbonic acid gas and at the same time precipitate troublesome resins and proteid matters.

The system consists in conditioning the beer in cask or other suitable vessel with the aid of kraüsen or priming, gradually chilling and filtering.

The beer is racked into either butts, hogsheads, or glass-enamelled tanks, which will stand a good pressure, and 10 p.c. of kraüsen or sugar priming is added, the object being to force the beer rapidly into a vigorous after-fermentation. Kraüsen consists of beer in the first stage of fermentation, 24–44 hours after filtering. The kraüsen should be taken from a beer of the same type and original gravity as the beer to be conditioned. When the beer is in high condition, which usually takes six or seven days, it is slowly chilled by the most suitable means. If glass-enamelled tanks are used, these should be fitted with coils through which refrigerated brine is passed. In this way the complete process of conditioning, chilling, and clarification can be worked in the same tanks. If the storage plant does not lend itself to chilling in bulk, the vessels are either placed in a cold cellar and allowed to cool gradually to the required temperature or the beer is passed through a counter-current chiller in which the beer can be chilled to any temperature without loss of gas or waste of beer. After cooling, the beer is stored for another few days at a uniform temperature of 30°F. to allow it to clarify to a considerable extent. It is then filtered through a pulp filter and bottled in a suitable machine.

Beer produced by this method requires no carbonation, as the maturing and conditioning process itself furnishes quite sufficient gas for beer condition either in cask or bottle. It will also retain its brilliancy for a very long period at any temperature.

Great care should always be taken to thoroughly cleanse the pulp used in the filter, and there are several machines available which can be used for this purpose. Scrupulous cleanliness of the whole plant as well as the bottles is most important.

Certain improvements have been designed of late years in the brewing industry, and are known as follows: 1. The Schneifle-Hill Patent brewing system. The claims of this process are that neither tropical nor arctic temperatures exert any after-influence on the stability, brightness, and palate flavour of the beers produced under this process. Among some of the improvements in this system may be noted the retention of the natural gases of fermentation in the beer, together with those exquisite flavours of the ethers and other volatile products (which are always wasted by the ordinary methods of brewing) to the ultimate benefit to the beer in palatefulness, and condition. The fermentations, however, are conducted precisely in the same manner as the ordinary top-fermentation system.

The albuminoids, also a most frequent cause of trouble, are dealt with by a most unique but simple clarifying system, whereby these undesirable constituents of malt worts are totally eliminated. It has been found by practice that from two to six days are required to bring about these results, by which time the beer is thoroughly matured, and ready for filling into the trade casks. In conjunction with the above advantages of always being able to supply the same and uniform beer throughout the year, must be added the great advantage of the reduced cost of production. It is a point which must appeal to all brewers in these days of severe competition and high prices of materials. Beers produced by this process can be brewed with 2 lbs. less original gravity, and still retain

the same palatefulness. Less hops can also be used at the rate of 1½ lbs. to 2 lbs. per quarter.

There is no waste or returns from the tenants. Finings are dispensed with, no cellar room is required in the brewery, as the beer is loaded on to the drays immediately after racking. There is a great saving of time and labour over the older system, with its drawing-off, topping-up, and general care and attention on the floors.

2. The choice of an appropriate name for an entirely new article of manufacture is always attended with difficulty, for although the adoption of a name of some kind or other is an easy matter, it is imperative that the name selected be a compendious one, capable of affording some indication of the nature of the product. This is more especially the case when the article is one designed for human consumption. Within the last few years there has been introduced into the brewing world an article termed 'concentrated beer.' The article is a semi-solid one, for the reason that the concentrated beer is the product of the brewer's art, and is a finished product, which needs only the addition of water to convert it into a beverage.

Innumerable attempts to concentrate finished beer have been made, but these have always ended in failure, as in the nature of things they must end, for the reason that the concentration of beer involves both the initial expense of producing a completely finished article, which is subsequently partially destroyed, as well as the cost of separating by evaporation 95 p.c. of the liquid, causing loss of aroma, and the destruction of the 'palate' or flavour of the beer. The converse is the case in producing the concentrated beer, for all the aroma is retained, the palate improved, and the beer made from the concentrate rendered more wholesome than ordinary beer.

To make one barrel of beer from the concentrate, a tin of the concentrated wort is dissolved in boiling water, and introduced into a 36-gallon cask, or, if more convenient, a covered vat of about the same capacity. The wort is now cooled down to 60°F., and about 1 lb. of pressed yeast is added. At the end of a few hours fermentation takes place, which is finished at the end of a week. The beer is now ready for drinking, and may be drawn off by means of a tap into clean bottles for storage if desired. The 36-gallon cask will fill 24 dozen pint bottles.

J. H.

BRIDELIA BARK or **ASDUANA.** The bark of *Bridelia montana* is a useful Indian astringent (Dymock, Pharm. J. [3] 7, 309).

BRILLIANT ARCHIL, -AZURINE, -BLACKS *v.* AZO- COLOURING MATTERS.

BRILLIANT CONGO, -CROCEÏN, -DOUBLE SCARLET, -GERANINE *v.* AZO- COLOURING MATTERS.

BRILLIANT COTTON BLUE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BRILLIANT GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BRILLIANT ORANGE, -PONCEAU, -PURPURINE, -SCARLET *v.* AZO- COLOURING MATTERS.

BRILLIANT YELLOW *v.* AZO- COLOURING MATTERS.

BRIMSTONE *v.* SULPHUR.

BRINDONIA INDICA *v.* GARCINIA INDICA.

BRIQUETTES *v.* FUEL; also PITCH.

BRITANNIA METAL. Is an alloy of variable composition, usually containing only tin and antimony, although brass and bismuth are sometimes added.

An alloy consisting of 9 parts of tin and 1 part of antimony is attacked slightly by solutions of common salt, potassium, ammonium, and magnesium chlorides, potassium sulphate, potassium nitrate, and sodium carbonate. Caustic soda has a more marked action (Dingl. poly. J. 221, 259).

This alloy is used in the manufacture of teapots, spoons, and dish-covers.

Articles made from it may be coloured by heating them for 15 to 30 minutes in a bath made by mixing 2 lbs. of water, 1½ oz. of cream of tartar, ½ oz. of tartar emetic, 2 oz. of hydrochloric acid, ¼ lb. of pulverised zinc, and 1 oz. of powdered antimony. This gives them a brilliant lustre.

By heating in a bath composed of 1 part tartar emetic, 1 part cream of tartar, 3–4 of hydrochloric acid, and 3–4 of ground antimony, the following tints may be obtained: golden, copper-red, violet, and blue-grey.

A metallic ring can be given to articles made of Britannia metal by heating them in an oil-bath to 220° and then cautiously raising the temperature to below 3° above the fusing point of the alloy. Small articles must be kept at this temperature for from 15 to 30 minutes, large articles for one hour; the bath is then allowed to cool. The rapidity of the cooling seems to have no appreciable effect (D. Ind. Ztg. 1867, 507) (*v.* ANTIMONY).

BRITISH GUM *v.* DEXTRIN.

BROCHANTITE. A hydrated basic copper sulphate, $CuSO_4 \cdot 3Cu(OH)_2$, forming bright-green orthorhombic crystals, found in Cornwall, Urals, &c. It is largely present in some of the Chilian copper ores. L. J. S.

BRÖGGERITE. A crystallised variety of the mineral pitchblende or uraninite, found as small, isolated octahedra and cubo-octahedra in the felspar quarries near Moss in Norway. It contains about 80 p.c. uranium oxide, together with thorium, lead, &c. *Cleveïte* is a very similar, or identical, mineral found in the felspar quarries near Arendal in Norway. L. J. S.

BROMAL. Tribromacetaldehyde CBr_3CHO. Prepared by passing bromine into a solution of paraldehyde in ethylacetate (Pinner, Annalen, 179, 68), or by passing bromine into absolute alcohol, fractionally distilling the product, and treating the fraction boiling at 165°–180° with water. The bromalhydrate thus formed is decomposed on distillation into bromal and water (Schäffer, Ber. 1871, 366; Löwig, Annalen, 3, 288). Bromal is an oily liquid boiling at 174° (760 mm.); sp.gr. 3·34. Alkalis decompose it on heating into bromoform and a formate.

Bromalhydrate $CBr_3CH(OH)_2$. Crystallises from water in colourless monoclinic prisms containing one molecule of water of crystallisation, m.p. 53·5°. It is less soluble than choralhydrate (Pope, Chem. Soc. Trans. 1899, 460).

Bromal alcoholates. Bromalethylalcoholate is a crystalline solid, m.p. 44°; readily soluble in alcohol, sparingly soluble in water (Schäffer, *l.c.*). Étard (Compt. rend. 114, 753) has described the action of bromine on various alcohols

with the formation of different bromal alcoholates.

The following condensation products of bromal have been prepared: *Bromalammonia* (Schiff and Tassinari, Ber. 1877, 1786); compound with *hexamethylenetriamine* (Lederer, Eng. Pat. 17693; J. Soc. Chem. Ind. 1897, 1039); compounds with *formaldehyde* (Pinner, Ber. 1900, 1432); *bromaldiacetate* (Grabutti, Gazz. chim. ital. 1900, 30, ii. 191); *bromalglycolate* (Gabutti, Chem. Soc. Abst. 1902, i. 261); and *bromalchloralcarbamide* (Kalle and Co., Chem. Soc. Abstr. 1902, i. 429).

BROMALIN. Trade name for a combination of hexamethylenetetramine with ethylbromide used in the treatment of neurasthenia and epilepsy (*v.* SYNTHETIC DRUGS).

BROMBENZENE *v.* PHENYL.

α-BROMCARMINE and **β-BROMCARMINE** *v.* COCHINEAL.

BROMCHINAL, BROMETONE, BROMEIGON *v.* SYNTHETIC DRUGS.

BROMINE. Sym. Br. At. wt. 79·92. An element belonging to the class of the halogens; discovered by Balard in 1826. Name from βρῶμος, a stench. Never found free; chiefly in combination with alkalis and alkaline earths. As AgBr, in Mexico and Chili, in some Silesian zinc ores, and in Chili saltpetre. In sea-water (in the ratio of 340 mgms. Br to 100 grams Cl) probably as magnesium bromide; in many marine plants and animals, and in many saline springs. Bromine, as bromindigo, has been found to be secreted by certain species of *Murex*, and is an essential constituent of the Tyrian purple of the ancients. Traces of it are occasionally to be met with in coal, and hence in gas liquors.

At ordinary temperatures is a dark brown-red liquid of most irritating smell, very volatile; vapour yellowish-red, and becoming less transparent when heated.

Boils at 63° and solidifies at −7·3° to a brown-red crystalline mass of semi-metallic lustre and conchoidal fracture.

Vapour acts on mucous membrane and occasions great irritation. Sp.gr. of liquid 3·18828, 0°/4° (Thorpe).

A solution of bromine in water, *bromine water*, contains when saturated 3·169 p.c. at ordinary temperature, and has a sp.gr. of 1·02367; it deposits when cooled *bromine-hydrate* $Br_2 10H_2O$ in hyacinth-red octahedral crystals. The solution is frequently used in analysis as an oxidising agent. Very soluble in alcohol, ether, carbon disulphide, chloroform, and conc. hydrochloric acid; sulphuric acid dissolves traces only.

Bromine acts violently on hydrogen, sulphur, phosphorus, arsenic, antimony, tin, the heavy metals, and potassium; but it does not react with sodium, even on heating to 200°. Acts as a bleacher and disinfectant.

Extraction and *Manufacture.*—Bromine occurs in nature principally, and so far as its industrial preparation is concerned, exclusively in the shape of bromides, accompanying in small quantities the chlorides of sodium, calcium, and magnesium. Its quantity is never large enough to admit of its being prepared directly from the raw material, but where the latter is in the first instance worked for sodium chloride and other salts, the bromide accumulates in the mother liquors, and can be recovered from these. Thus Balard discovered bromine in the mother liquors obtained on making common salt from sea-water, and for many years it was prepared from the mother liquors of the saltworks at Kreuznach, Schönebeck, Neusalzwerk, and other places in Germany. It was also found in 1846, by Alter, in similar mother liquors in America, especially in those at Natrona and Tarentum, later on at Pittsburg, Syracuse, Pomeroy (Ohio), and in the Kanawha region in West Virginia (Mason City, Parkersville, &c.).

Until about 1860 the little bromine that was made was nearly all used for scientific purposes. Then, however, medicine and photography began to demand a greater supply of bromides, and later on the manufacture of coal-tar dyes raised an even more extended demand for bromine. It now became remunerative to recover it in the working up of kelp for iodine, but this yielded only little and impure bromine, and was not long continued. An idea was conceived of recovering it from the water of the Dead Sea, but the project, hardly practicable in itself, was abandoned when Frank had shown that an ample supply of bromine could be obtained from the mother liquors of the Stassfurt potash industry (*v.* POTASSIUM CHLORIDE). He commenced his practical operations in 1865, when he manufactured about 750 kgs. of bromine; in 1867 the output had already increased to 7½ tons, and in 1885 the Stassfurt production of bromine was estimated at 260 tons per annum, the price having gone down from 50 or 60 (sometimes as much as 90) marks per kilogram to 0·70 mark. This lowering of the price was principally due to the fact that since 1868 the Americans had come into the market with bromine made from the above-named saltworks; their liquors contained it in such quantity that they are able to sell much below Stassfurt prices.

Few substances have so rapidly diminished in price. Originally costing from 90 to 95 marks per kg., the price fell in 1867 to 40–45 marks, then to 12 marks, later to 2·30 marks, 1·25 and 0·70 mark. It is now about 1·60 marks. The world's production is now practically controlled by the 'Associated American Producers,' and the 'German Bromine Convention,' in Stassfurt Leopoldshall.

Chemical Processes.—The raw material worked at Stassfurt, crude carnallite (*v.* POTASSIUM CHLORIDE), contains bromine to the extent of from 0·15 to 0·25 p.c. in the shape of *brom-carnallite* $MgBr_2 \cdot KBr, 6H_2O$, isomorphous with carnallite. In the manufacture of potassium chloride, the magnesium bromide accumulates together with magnesium chloride in the mother liquors, which contain usually from 0·2 to 0·3 p.c. bromide. As it is impossible to separate the magnesium bromide by fractional crystallisation, the bromine is always extracted chemically, being replaced by a current of chlorine, according to the equation:

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

The chlorine is either generated within the liquors by means of hydrochloric acid and manganese ore, or it is prepared outside and passed into the solutions, cheap compressed chlorine in steel cylinders being nowadays available for that purpose.

In the early days of the bromine industry, the extraction was always done by intermittent working. One of the first apparatus employed was devised by Frank, and is shown in Fig. 1. It consisted of a square vessel or still, A, made of sandstone or slate properly jointed together, of about 3 cubic metres capacity, which was charged with a definite quantity of mother liquor previously heated to 60° in tank B by steam coil *i*; about 200 kgs. of manganese ore, sufficient for several operations, were spread on the false bottom *a*. After closing the man-hole *f*, the required quantity of sulphuric acid of sp.gr. 1·7 was run in through pipe *g*, which was subsequently stopped up with clay, and live steam was passed into the liquor through pipe *k*. The chlorine evolved on boiling acted upon the magnesium bromide present and liberated bromine. This came over pure at first, but above 75° a mixture of bromine, chlorine, and water vapour passed through the lead pipe *h* and the stoneware condensing coil C into the glass bottle D,

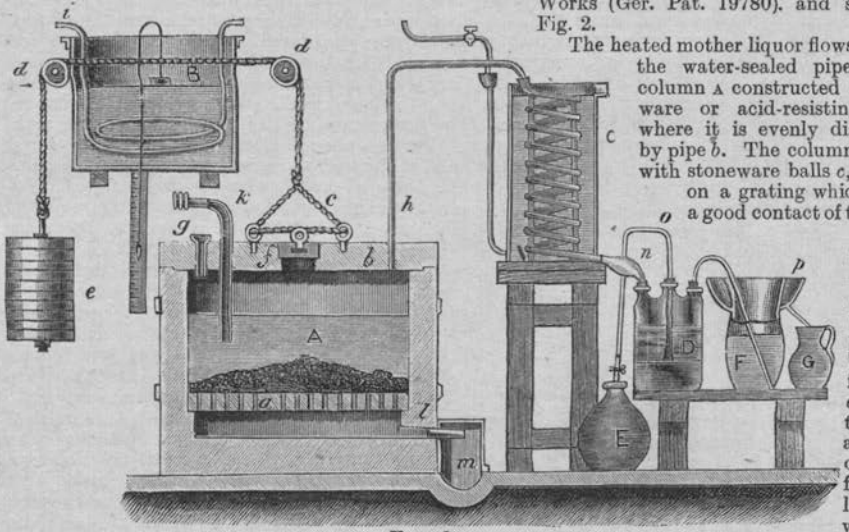


FIG. 1.

holding about 8 litres. The distillation was carried on until the pale colour of the vapours in the glass adapter *n* showed that no more bromine was coming over. The condensate separated into a lower layer of bromine and an upper layer of bromine and chlorine water which could be siphoned off through *o* into vessel E, and was added to a subsequent charge. Uncondensed vapours passed into vessel F filled with iron turnings and water, and fitted with a collar, *p*, to allow for frothing, with a run-off into jar G. Each operation, lasting an hour to an hour and a half, was terminated by knocking out plug *l*, and running off the liquor through the covered culvert *m* connected to the factory chimney.

The efficiency of this process was very small, each operation yielding 2 to 2·5 kgs. bromine, the average yield amounting to not more than 0·1 p.c. of the mother liquor. The intermittent method entailed several drawbacks—loss of time and material, besides the contamination of the atmosphere. These disadvantages gave rise to various continuous processes, the first of which was patented by Frank in 1878.

He employed a series of decomposing vessels at different levels, allowing the heated liquor to run from the highest into the next lower one, and so on, passing at the same time chlorine gas generated outside and steam into the lowest vessel, and in counter-current to the higher ones. He thus obtained a steady stream of bromine on the one hand, and a solution of magnesium chloride practically freed from bromine and uncontaminated with manganese salts, on the other. After a time, chlorine was passed into the second lowest vessel, and steam only into the lowest, to free its contents from chlorine before running off. However, the high pressure required to force the chlorine gas through several successive layers of the liquor presented great difficulties in the design and working of this plant. These were overcome by the application of the scrubber principle in the apparatus, patented in 1882 by the Leopoldshall Chemical Works (Ger. Pat. 19780). and shown in Fig. 2.

The heated mother liquor flows through the water-sealed pipe *a* into column A constructed of stoneware or acid-resisting stone, where it is evenly distributed by pipe *b*. The column is fitted with stoneware balls *c*, *c* resting on a grating which effects a good contact of the liquor with the chlorine gas ascending through pipe z. This pipe is wide enough to serve also as outlet for the liquor which runs into the steaming vessel B, provided with a number of superimposed flagstone shelves compelling the liquor to flow in a zigzag course, and finally issues through pipe *i*. Steam is forced into this vessel by means of a stone pipe *g* and is distributed through perforations in its base. The contents of B, which is always full, are kept boiling, and the steam rises principally through holes in the flagstones, thereby freeing the liquor from chlorine and bromine. The vapours meet the current of fresh chlorine arriving through pipe *l* (shown in dotted lines), which is conveyed through pipe z into the tower A, decomposing the magnesium bromide. The bromine is taken off on top, and passed by pipe *o* through the stoneware condenser *p* into the receiver *q*. The uncondensed vapours are led through *x*, into receptacle *n*, and arrested in the smaller scrubber *d* suspended by rod *t*, and fitted with iron borings, kept moist by a stream of water from tube *f*. The iron bromide collected in *n* is siphoned off through *v* into jar *w*. The regularity of the

current of chlorine arriving from *m* is controlled by the amount of water condensing in the bend of the glass tube *h*. If too much water has accumulated, it is blown through the rubber tube *u* into the chlorine washer D. By filling the bend of *h* with water, the current of gas may be interrupted. Of late years chlorine electrolytically prepared and compressed in steel cylinders has been used, whereby the regularity of the current is under complete control.

The apparatus patented by Wünsche-Sauerbrey (Ger. Pat. 158715) is based on the same principle as the foregoing. It is, however, technically more perfect and consequently much superior in efficiency.

It consists of a decomposing vessel, a steaming vessel, a condenser, and an auxiliary condenser. The four units are built up of cast-iron elements of hexagonal cross-section, lined with stoneware plates and filled with a very large number, several thousands, of specially designed contact bodies which rest on gratings of the same material. The four units are so arranged in height that a perfect counter-current is obtained, and in both the decomposer and condenser two centre gratings are provided, in order to keep a free space. The chlorine is passed into the decomposer, the liquor after treatment in this unit runs into the steaming vessel, where it is freed from chlorine and bromine vapours by means of live steam, the vapours passing into the free space of the decomposer. The bromine leaves the decomposer and undergoes preliminary cooling in the auxiliary condenser, but is completely condensed in the principal condenser by a stream of water, passing subsequently a bromine and water separator.

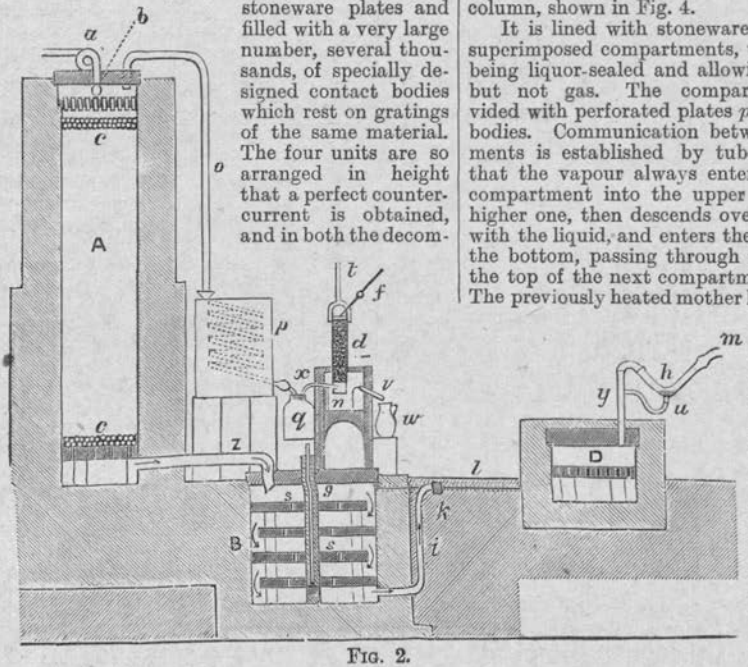


FIG. 2.

The features of this apparatus are the complete recovery of bromine and the thorough utilisation of steam. Although of moderate dimensions, the apparatus is capable, on account of the number and arrangement of contact bodies, to recover 250–270 kgs. bromine from 150 cub. m. liquor in 24 hours. It requires 0·6 kg. chlorine for every kg. of bromine made, and only 3 to 5 kgs. bromine are necessary in the form of iron bromide for the subsequent removal of chlorine from 100 kgs. crude bromine. The cost of production of 1 kg. bromine is 0·45 to 0·50 mark.

Whilst the value of Wünsche's apparatus depends on the most favourable distribution and utilisation of gas and liquor, Kubierschky has designed a plant (Ger. Pat. 194567) in which the counter-current proper is divided into a number of systematically arranged parallel currents, recognising the fact that bromine vapour will be heavier the purer it becomes. As the ratio of the density of water to that of bromine is 18 : 160, a simple upward current cannot possibly yield the best separation, as under-currents will always be set up.

The apparatus consists of a single tower column, shown in Fig. 4.

It is lined with stoneware and divided into superimposed compartments, the division plates being liquor-sealed and allowing liquid to pass, but not gas. The compartments are provided with perforated plates *pp* or other contact bodies. Communication between the compartments is established by tubes *rr* so arranged that the vapour always enters from the lower compartment into the upper part of the next higher one, then descends over the plates along with the liquid, and enters the vapour pipe near the bottom, passing through this pipe again to the top of the next compartment, and so forth. The previously heated mother liquor enters at the top of the column, runs down in a direct course and is met by chlorine introduced in the lower part. Steam is passed into the bottom compartment, and follows the course described. The bromine, not subjected to under-currents, issues at *a* from the column and is condensed in an earthenware coil.

Although of extreme simplicity, this apparatus is much superior to all the others, especially in regard to yield, this amounting to from 90 to 95 p.c. of the bromide present in the crude liquors.

Electrolytic Processes.—Of recent years, efforts have been made to effect the separation of bromine from the magnesium-bromide liquors by means of electrolysis. A number of processes have been devised by Wünsche, Höpfner, Nahnsen, Pemsel, Rinck, Dow, and Kossuth, but although in some cases plants have been working with more or less success, their introduction has, in Europe at any rate, not become general. All but the last-named process employ diaphragms, to avoid secondary reactions. Kossuth works without this, and achieves a great simplicity of plant and working, but at the expense of current required. The yield of electric energy is 40–50 p.c. in his case, and

not more than about 70 p.c. in any other method. This low yield is largely due to the extremely small percentage of bromine in the liquors and the consequently large bulk to be dealt with, and to the formation of bromates and chlorates. The formation of solid magnesia is another drawback.

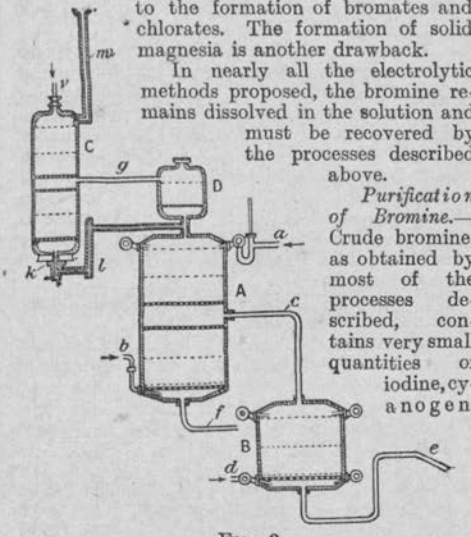


FIG. 3.

In nearly all the electrolytic methods proposed, the bromine remains dissolved in the solution and must be recovered by the processes described above.

Purification of Bromine.—Crude bromine, as obtained by most of the processes described, contains very small quantities of iodine, cyanogen, bromoform and carbon tetrabromide, lead bromide, and as principal impurity from 1 to 4 p.c. of chlorine as chloride of bromine. The oldest method of purification consisted in agitating the crude bromine with a solution of potassium or ferrous bromide. On account of the frequent breakages of the glass vessels employed, this method was replaced by that of redistillation. In some places glass retorts were used for this purpose, containing about 15 kgs. and heated in sand-baths. Only 3 or 4 charges could be worked in one vessel, and fracture of the retorts was a not unfrequent occurrence. In Stassfurt sandstone stills were and are still employed. These were square troughs with a stone cover, holding about 1 cubic metre. The distillation is carried out in the presence of ferrous or calcium bromide, these liquors being, when used up, added to the original mother liquors. Of late years advantage has been taken of the improved products of the stoneware industry, and stills of this material are largely used. To avoid the occasional cracking of these stills, Mitreiter employs vessels of boiler plate lined with a bromine resisting material.

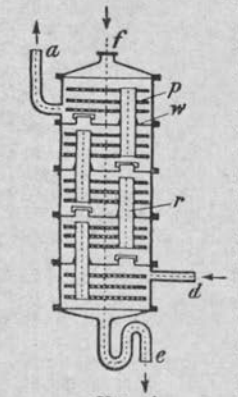


FIG. 4.

The still is charged with 200 litres ferrous bromide solution of 13° to 18°Bé, and about 600 litres crude bromine. The temperature is gently raised by direct steam up to the boiling-point. Double decomposition ensues between chlorine and ferrous bromide, and bromine distils over and is condensed in a stoneware coil, separated from water and then contains only from 0·05 to 0·10 p.c. chlorine.

Recent processes attempt the purification by rectifying without the aid of chemical agents. Kubierschky (Ger. Pat. 174848) employs in connection with his separating apparatus a refining tower; the crude bromine flows downwards into a vessel charged with bromine and kept at boiling temperature. The chlorine rises in the tower, and the boiling bromine, freed from chlorine, is continually siphoned off and cooled.

The German Solvay Works (Ger. Pat. 205448) have found that in raising the temperature of crude bromine very slowly and keeping it just under its boiling-point, it is possible to free it entirely from its chlorine. The time factor is of great importance for the successful carrying out of their process.

On heating a charge to 59° for 36 to 40 hours, it is possible to remove practically all the chlorine with not much more bromine than corresponds to the composition of bromide of chlorine.

Bromine is sold in strong, white, stoppered bottles, holding 1 litre, and containing 2½ or 3 kilos. The glass stoppers must be well ground; they are secured by pouring some shellac on to the joint, covering them with clay putty, and tying wet parchment paper over all. From four to twelve such bottles are placed in a wooden box, the spaces between being tightly filled with kieselguhr or brown-coal ashes, depending upon whether the bromine is exported or sold for inland consumption.

The principal applications of bromine, whether in the free state or in the shape of bromides, are in photography, in medicine, in the manufacture of coal-tar dyes (especially eosine), and in scientific and analytical chemistry; in the latter it has to a great extent taken the place of chlorine, owing to the greater convenience of its manipulation. A similar substitution has been proposed for many technical purposes. It is used in the extraction of gold and the refining of platinum, and in connection with the manufacture of Prussian blue and potassium permanganate. It is also a disinfectant, and has found some application for this purpose, especially in the shape of *bromum solidificatum* patented by Frank (Ger. Pat. 21644). This is kieselguhr made plastic by means of molasses, &c., pressed into sticks of ¼- and ½-inch diameter, dried, burned to the extent that the sticks acquire a sufficient degree of hardness without losing their porosity, and saturated with liquid bromine in wide-mouthed stoppered glass bottles. After the excess of bromine has been poured off, the sticks remain behind, containing about 75 p.c. of the weight of bromine, and are sold in the same bottles. This is a very convenient form of applying it, as a certain number of sticks represent a given weight, and no weighing out of liquid bromine is required.

Bromide of iron is made at Stassfurt, and serves principally as raw material for the manufacture of potassium and sodium bromide. It is a compound of the formula Fe_3Br_8, containing 56–70 p.c. bromine, up to 0·5 chlorine, 18–19 p.c. iron, and 10–15 p.c. water and insoluble matter. The older method for its manufacture consists in passing bromine vapours free from chlorine over iron borings or turnings

contained in a cast-iron or stoneware vessel, and kept moist by a stream of water. The solution obtained is passed through a filter cloth or sand filter to remove impurities, notably carbon, and evaporated in cast-iron pans, whereby enough bromine is added to obtain the compound Fe_3Br_8. The brown-red solution is concentrated to a pasty consistency and allowed to cool to a black crystalline mass.

The Associated Chemical Works of Leopoldshall have introduced a method whereby a charge of 1 ton of steel wire and turnings is treated in a closed stone trough with a mixture of bromine vapour and steam in the right proportion. The admission of bromine is so regulated that no bromine vapours are visible through a sight-glass provided on the outlet pipe which is connected to a little scrubber acting as a catch-box. As soon as brown vapours and the falling of the temperature from 170° to 100° indicate a lessening of the activity of the iron, the operation is terminated and the solution run off. Being sufficiently concentrated, the solution obtained in the process may be run direct into the transport barrels, where it is allowed to crystallise.

Bromine salt. In connection with the manufacture of bromine a substance commonly called 'bromine salt' is produced which finds application in the extraction of gold ores. It is practically the mixture $NaBrO_3+2NaBr$, and is made by saturating concentrated caustic soda solution with bromine. The solid salt obtained after draining off the mother liquor—which is evaporated—has the approximate composition $1NaBrO_3+5NaBr$. To this sodium bromate, electrolytically prepared from bromide, is added, and the mixture finely ground and packed in kegs.

Hydrobromic acid. HBr. *Bromhydric acid; Hydrogen bromide.* A colourless pungent gas of irritating smell; fumes strongly in the air. Condenses to a liquid at −73°. May be obtained synthetically by passing bromine and hydrogen through a hot tube or over heated platinum. Best prepared by action of phosphorus and bromine on water, $5Br+P+4H_2O=H_3PO_4+5HBr$; or by the action of a concentrated solution of H_3PO_4 on KBr; or by dropping Br upon melted paraffin heated to 185°.

Gas very soluble in water; solution when saturated forms a colourless, strongly acid liquid of sp.gr. 1·78, and contains 82 p.c. HBr by weight, corresponding to the formula HBr,H_2O. If the concentrated acid be heated at ordinary pressures, the gas is evolved until the amount of HBr in the solution sinks to 47–48 p.c., when the liquid boils constantly at 126° under a pressure of 760 mm. This proportion of HBr corresponds to $HBr+5H_2O$, but the liquid is not a true hydrate, since the composition is altered by varying the pressure; thus if the pressure be raised to 1·95 mm., the solution boils at 153° and contains 46·3 p.c. HBr.

The sp.gr. at 15° and p.c. composition of aqueous solutions of hydrobromic acid, is given in the following table (Wright, Chem. News, 23, 242):—

Sp.gr.	HBr p.c.	Sp.gr.	HBr p.c.
1·080	10·4	1·385	40·8
1·190	23·5	1·475	48·5
1·248	30·0	1·515	49·8

For pharmaceutical purposes a dilute solution of hydrobromic acid may be prepared by dissolving 84½ grains of potassium bromide in a fluid ounce of water and adding 9 grains of tartaric acid to the solution. After standing, acid potassium tartrate crystallises out and the solution contains about 10 p.c. of hydrobromic acid. Hydrobromic acid has been used in the treatment of ear complaints. R. L.

BROMIPIN. A combination of bromine with sesame oil employed in medicine (*v.* SYNTHETIC DRUGS).

BROMITE or BROMYRITE. Native silver bromide, found in Mexico and in Chili (*v.* SILVER).

BROMOCOLL *v.* SYNTHETIC DRUGS.

BROMOFORM. *Tribrommethane* $CHBr_3$. This substance is occasionally met with in the liquid left after the rectification of bromine, in which it occurs associated with *chlorobromoform* $CHBr_2Cl$ (Dyson, Chem. Soc. Trans. 43, 46) and *carbon tetrabromide* CBr_4 (Hamilton, *ibid.* 39, 48).

Preparation.—It may be obtained by mixing 100 c.c. soda lye, 200 c.c. acetone, and 20 c.c. bromine. When the reaction has ceased, 10 c.c. acetone are added to remove the yellow colour of the hypobromite, the layer of bromoform which separates being tapped off and rectified. Yield 75 p.c. (Denigès, J. Pharm. Chim. 24, 243). It may also be prepared by the simultaneous action of bromine and caustic potash on alcohol, of bromine and lime on acetone (Beniger, Amer. J. Pharm. 63, 80); of calcium hypochlorite and potassium bromide on acetone (Fromm, Pharm. Zeit. 39, 164), and by the action of alkalis on bromal. It has been made electrolytically from potassium bromide and alcohol (Fabrik vom Schering, D. R. P. 29771); from potassium bromide and acetone (Coughlin, Amer. Chem. J. 27, 63; and Müller and Loebe, Zeit. Elektrochem. 10, 409), and from calcium bromide, alcohol, and water (Trechcinoki, Chem. Zentr. 1907, i. 13).

Properties.—It is, when pure, a colourless liquid, solidifying at 9° and boiling with slight decomposition at 146° under 751 mm. (Wolff and Schwabe, Annalen, 291, 241), at 151° under ordinary pressure. Sp.gr. 2·902, 15°/15° (Perkin, Chem. Soc. Trans. 45, 533). It is decomposed by potash into potassium bromide, hydrogen bromide, and carbon monoxide, and may be estimated by means of this decomposition (Desgrez, Compt. rend. 125, 780, and Annalen 23, 76; and Richaud, J. Pharm. Chim. 1899, 232). Under the influence of light and air it decomposes, the decomposition products depending on the time of exposure and the amount of available oxygen (Schoorl and Van den Berg, Chem. Zentr. 1906, i. 441). It has been used to a slight extent as an anæsthetic, and in the treatment of diphtheria. Bromoform in water to which a little alcohol has been added, has been successfully used in cases of whooping-cough complicated with pneumonia (Stepp and Goldschmidt, J. Soc. Chem. Ind. 1890, 213).

BROMOL, BROMOLEIN, BROMOTAN *v.* SYNTHETIC DRUGS.

BROMURAL. Trade name for *α-monobromisovalerianylurea.* Employed as a hypnotic. Forms white needles, slightly bitter in taste; readily soluble in hot water, alcohol, and ether, sparingly soluble in cold water; m.p. 147°.

BRONZE *v.* TIN.

BRONZE POWDERS. The manufacture of these powders is carried on largely at Fürth and Nuremberg in Bavaria. Bronze powders are composed of copper, zinc, tin, and antimony, melted together in the requisite proportions. In the process of manufacture, the alloy is cast into rods ½ inch in diameter and 3 feet long. These are rolled until about 2 inches wide, and then cut into lengths suitable for handling. The pieces are hammered out thin, and cleansed by immersion in dilute sulphuric acid. The dried material is then beaten out by steam-hammers until the limit of thickness is reached, when it is cut up by shears into small particles or 'clippings.' These are then pulverised in stamp mills, and the powder sifted, to separate the heavier and better quality powder from inferior material. The latter is mixed with quartz powder and sold very cheaply (J. Soc. Chem. Ind. 1893, 12, 475).

The expense of the above process lies mainly in the production of 'clippings,' which necessitates a great deal of handwork, and a number of methods have been patented for reducing the alloy to a finely divided state by mechanical means. According to one method, the molten alloy is rained into a sheet-iron chamber, in which a shaft carrying blades is rapidly rotated, so as to greatly agitate the air and thereby minutely subdivide the metal at the moment of solidification (Fr. Pat. 331371, 1903). In another, the molten metal flows in a thin film into a receptacle, where it meets a current of compressed air or else a jet of water, the object being to produce bronze foil or leaves (Eng. Pat. 9064, 1903). Methods have also been patented for casting the metal in thin films on the inner surface of a rotating hollow cylinder or in the annular space between two rotating cylinders (J. Soc. Chem. Ind. 1903, 22, 150; Fr. Pat. 335112, 1903).

After the powdered metal has been sifted, the coarser grades are polished in a closed steel cylinder, in which steel wire brushes rub against the walls. When it is necessary to reduce the powder to a finer state of division, it is rubbed with gum-arabic solution, washed and dried at the lowest possible temperature.

Zinc-dust is frequently coated with brass by simple immersion in a copper and zinc cyanide solution, the powder being kept agitated by means of brushes (J. Soc. Chem. Ind. 1894, 13, 893, 958); the product is treated finally in a polishing mill, and used as a bronze powder.

Bronze powders have also been described containing 5–10 p.c. of aluminium, and 0·05–0·1 p.c. of bismuth. The shade of colour is altered by varying the percentage of aluminium, and by heating in air (D. R. P. 44242, 1887).

Few analyses of bronze powders have been published (J. Soc. Chem. Ind. 1910, 29, 1062). 'Gold' and 'bronze' powders were found to contain 70–85 p.c. of copper, and 30–15 p.c. of zinc, together with small amounts of lead, tin, arsenic, iron, and aluminium; 'aluminium' powders consist of nearly pure aluminium; and 'silver' powders contain 77 p.c. of zinc and 21·5 p.c. of aluminium.

Bronze powders are coloured in various ways. One method consists in heating the powder in an open vessel with oil and vinegar, or with wax, paraffin, or oils containing sulphur. Buchner's process consists in shaking the powder in a closed vessel with hydrogen sulphide solution, allowing to stand 24 hours, drying and heating in an oil-bath until sufficiently coloured (J. Soc. Chem. Ind. 1896, 15, 283). Artificial dyestuffs are also used for colouring bronze powders.

The following are examples:—

Colour of powder	Metallic constituents	Total organic matter	Colouring matter
Pink . .	Copper . .	0·3 p.c.	Azine scarlet G
Blue . .	Tin and zinc .	3·8 ,,	Victoria blue 4R
Copper colour	Copper (little zinc)	5·5 ,,	Safranine
Violet. .	Tin (little copper)	3·8 ,,	Fast neutral violet B
Pale green .	Copper and zinc	4·3 ,,	Malachite green
Olive green .	Copper and zinc	5·9 ,,	Brilliant green

Bronze powders are used considerably for printing on textile fabrics. For this purpose, they must be mixed with a 'fixer' which allows the powder to be readily applied to the material, whilst so fixing it that brushing will not remove it; the fixer must not, of course, interfere with the brilliancy of the powder. Two classes of 'fixers' are in use, egg or blood albumen, and various varnishes having caoutchouc as their base. In printing such goods, the main point to be observed is that the impression shall be sharp, and applied with sufficient force to prevent the particular fibres from again rising. (For further particulars, *v.* J. Soc. Chem. Ind. 1896, 15, 283; 1900, 19, 243; 1906, 25, 1040; and for various bronze powder substitutes, *v. ibid.* 1896, 15, 284.)

BROOKITE *v.* TITANIUM.

BROOM TOPS. *Scoparius.* (*Genêt à balais*, Fr.; *Besenginster*, Ger.) The tops of the common broom, *Cytisus scoparius*, Link (Bentl. a. Trim. 70), have been employed for their diuretic and purgative properties since the Anglo-Saxon period, and are noticed in nearly all the herbals and pharmacopœias. The old writers describe the broom under the name 'genista,' 'genesta,' or 'genestra,' and it was the wearing of the 'planta genista' as an emblem by Geoffrey, Count of Anjou, that gave the title 'Plantagenet' to his royal descendants (comp. Flück. a. Hanb. 170).

Stenhouse in 1851 discovered in broom tops a liquid alkaloid *sparteïne* $C_{15}H_{26}N_2$, together with a chemically indifferent crystallisable compound *scoparin* $C_{21}H_{22}O_{10}$ (Annalen, 78, 15). Sparteïne has been further investigated by Mills (Chem. Soc. Trans. 15, 1), Houde (J. Pharm. Chim. [5] 13, 39), Bamberger (Annalen, 235, 368), Coninck (Compt. rend. 104, 513), and Ahrens (Ber. 20, 2218; 21, 825). To obtain it Mills distils the tops with soda, separates the crude oil which comes over, acidifies it, and redistils with soda. The impure alkaloid is then dried in a current of hydrogen, the adhering soda removed, and finally it is submitted to fractional distillation. It is a viscid, colourless oil, with an unpleasant odour and bitter taste. It sinks in water, in which it is nearly insoluble. B.p. 188° (corr.), 18·5 mm.; 325° (corr.) in current of

dry hydrogen, 754 mm. (Moureu and Valeur, Compt. rend. 137, 194). With acids sparteïne combines, forming crystallisable salts: $B''(HCl)_2PtCl_4 2Aq.$, yellow crystalline powder (Mills); $B''(HCl)_2AuCl_3$ (Mills); $B''H_2SO_4$, large prisms, v. sol. water (Bamberger); B'HI, four-sided plates, sol. hot water (Bamberger); $B''(HI)_2$, silky needles (Bamberger). Sparteïne is a narcotic poison resembling nicotine, but less active (Stenhouse; *cf.* Sée, Compt. rend. 101, 1046). A characteristic orange-colour reaction is said to be produced when sparteïne or its salts are added to sulphydrate of ammonium (Grandval a. Valser, J. Pharm. Chim. [5] 14, 65).

The more important reactions of sparteïne are: 1. Nitric acid converts it into a compound which yields chloropicrin when treated with chloride of lime (Stenhouse).—2. Oxidised with potassium permanganate, it yields formic and oxalic acids (Bamberger; Ahrens).—3. Oxidised by peroxide of hydrogen, a new base, *dihydroxysparteïne* $C_{15}H_{26}N_2O_2$, is formed. It is syrupy, colourless, not crystallisable, and distils with difficulty with steam. Platinum salt $B''(HCl)_2PtCl_4$, blackens at 235°; and gold salt $B'(HCl)AuCl_3$ melts at 143°–146° (Ahrens).—4. Reduced by nascent hydrogen, a colourless oil, *dihydrosparteïne* $C_{15}H_{28}N_2$ results. It boils at 281°–284°, and forms a crystalline platinum salt $B''(HCl)_2PtCl_4$, which blackens at 239° (Ahrens).—5. With alkyl iodides and alcohol sparteïne reacts, forming $(C_{15}H_{27}EtN_2)I_2$ (Mills) and $(C_{15}H_{27}MeN_2)I_2$ (Coninck), which compounds by the action of oxide of silver yield the hydroxide $(C_{15}H_{27}EtN_2)(OH)_2$ (Mills), and by the action of soda $(C_{15}H_{26}N_2)EtI$ and $(C_{15}H_{26}N_2)MeI$ (Bamberger). Mills also obtained a diethyl di-iodide $(C_{15}H_{26}Et_2N_2)I_2$.—6. Heated with concentrated hydriodic acid at 200°, methyl in the form of methyl iodide is removed, and there remains a *new base* $C_{14}H_{24}N_2$, b.p. 276° (Ahrens). This, however, according to Herzig and Meyer (Monatsh. 16, 605), is only impure sparteine.—7. When sparteïne is distilled with lime the distillate contains ethylene, propylene, (γ)-picoline, and a new tertiary base (Ahrens).

Scoparin was obtained by Stenhouse from broom tops, after a series of processes to free it from the chlorophyll with which it is associated, as a pale-yellow powder which crystallises with difficulty. It is sparingly soluble in water, but is soluble in alcohol and alkalis. Its solution in ammonia is deep yellow-green. With chloride of lime a green colour is produced. Nitric acid converts it into picric acid. Melted with potash it gives phloroglucinol and protocatechuic acid (Hlasiwetz, Annalen, 138, 190). Recent investigations show that scoparin, which melts at 202°–219°, according as it is slowly or quickly heated, has the constitution $OH{\cdot}C_{19}H_{16}O_8{\cdot}OMe + 5H_2O$. It gives a violet-blue colour with ferric chloride, quickly becoming dark-brown, and reduces Fehling's solution (Goldschmidt and v. Hemmelmayr, Monatsh. 14, 202; 15, 316; A. G. Perkin, Chem. Soc. Proc. 1899, 123). Heated with alcohol a less soluble modification, *isoscoparin*, is formed, which is readily reconverted into scoparin by solution in alkali and precipitation by an acid (Stenhouse). *Iso*scoparin melts at 235° (Goldschmidt and v. Hemmelmayr). A. S.

BROSIMUM GALACTODENDRON (Don.). The latex of this urticaceous tree (cow-tree, milk-tree), growing in Venezuela, approximates to cow's milk in composition. It contains 35·2 p.c. of wax and saponifiable matters, which are used in the manufacture of candles (Boussingault, Pharm. J. [3] 9, 679).

BROUSSONETIA PAPYRIFERA (Vent.). *The Paper mulberry.* The fibrous bark is used in China and Japan for the manufacture of a kind of paper, and in Polynesia in the manufacture of Tapa cloth.

BROWN, ACID, *v.* AZO- COLOURING MATTERS.

BROWN, ANILINE; BISMARCK BROWN, MANCHESTER BROWN, PHENYLENE BROWN, VESUVINE, LEATHER BROWN, CINNAMON BROWN, ENGLISH BROWN, or **GOLD BROWN;** *v.* AZO- COLOURING MATTERS.

BROWN, ANTWERP, *v.* PIGMENTS.

BROWN, ARCHIL, *v.* AZO- COLOURING MATTERS.

BROWN, BONE, *v.* PIGMENTS.

BROWN, CALEDONIAN, *v.* PIGMENTS.

BROWN, CAPHEK, *v.* PIGMENTS.

BROWN, FAST, *v.* AZO- COLOURING MATTERS.

BROWN, FUSCANINE, *v.* AMINOPHENOL.

BROWN, GARNET. The potassium or ammonium salt of *iso*purpuric acid ($C_8H_4N_5O_6K$ or $C_8H_8N_6O_6$). Obtained by Hlasiwetz in 1859 by the action of potassium cyanide on picric acid (Annalen, 110, 289). Forms a dark-brown powder, readily soluble in hot water with reddish-brown colour. Dyes wool and silk brown in an acid-bath. No longer is use (*v.* also ISOPURPURIC ACID).

BROWN, MADDER, *v.* PIGMENTS.

BROWN, NAPHTHYLAMINE, *v.* AZO-COLOURING MATTERS.

BROWN, PHENYL, *v.* PHENYL BROWN.

BROWN, PICRYL, *v.* PICRYL BROWN.

BROWN, PIGMENT, *v.* AZO- COLOURING MATTERS.

BROWN, PRUSSIAN, *v.* PIGMENTS.

BROWN, RESORCIN, *v.* AZO- COLOURING MATTERS.

BROWN, SOUDAN, *v.* AZO- COLOURING MATTERS.

BROWN, VANDYKE, *v.* PIGMENTS.

BROWN, VERONA, *v.* PIGMENTS.

BROWN BERRIES. The fruit of *Rubus fruticosus.*

BROWN COAL *v.* FUEL.

BROWN HÆMATITE *v.* IRON, ORES OF.

BROWN IRON ORE (*Limonite*) *v.* IRON, ORES OF.

BROWN OCHRE. A soft variety of brown iron ore occasionally used as a pigment.

BRUCINE *v.* VEGETO-ALKALOIDS.

BRUCITE. Native magnesium hydroxide $Mg(OH)_2$, found as platy crystals with perfect micaceous cleavage, or as lamellar masses, in serpentine rocks, at Unst, one of the Shetland Isles, at Texas in Pennsylvania, &c. It sometimes contains a small amount of iron (ferro-brucite) or manganese (manganbrucite). A fibrous variety is called nemalite. L. J. S.

BRUNSWICK BLACK is prepared by fusing 2 lbs. of asphalt, and mixing thoroughly with 1 pint of hot boiled oil. When cool, 2 pints of turpentine are added to the mixture. An inferior but cheaper black may be made by boiling gently together for five hours 25 lbs. each of black pitch and gas tar asphaltum,

8 gallons of linseed oil, and 10 lbs. each of litharge and red lead are then mixed in, and the whole boiled. After cooling, the mixture is thinned by the addition of 20 gallons of turpentine (*v.* also BONE OIL).

BRUNSWICK GREEN. An oxychloride of copper, used as a pigment. Copper filings or turnings are moistened with a solution of sal-ammoniac, and left in contact with the air; the oxychloride so formed is washed off with water, and dried at a gentle heat. The term is also applied to chrome green and to emerald green (*v.* COPPER and PIGMENTS).

BRUSHITE. A hydrated phosphate of lime $HCaPO_4,2H_2O$ occurring in the guano of Aves Island and Sombrero in the Caribbean Sea.

BRUSSELS SPROUTS. A variety of the cabbage (*Brassica oleracea*), in which numerous small heads are developed along the stalk from the axils of the leaves, instead of one terminal head.

The edible portion contains, according to American analyses:

Water	Protein	Fat	Carbohydrates	Ash
88·2	4·7	1·1	4·3	1·7

(*see* CABBAGE). H. I.

BRYOIDIN *v.* OLEO-RESINS.

BRYONY ROOT. Contains a white, very bitter dextrorotary glucoside, *bryonin*, of the formula $C_{34}H_{48}O_9$, yielding by hydrolysis *bryogenin* $C_{14}H_{18}O_2$; m.p. 210°, dextrorotary $[\alpha]_D = +105°$, soluble in conc. sulphuric acid, forming a red solution changing to purple on heating, and giving a purple precipitate on the addition of water (Masson, J. Pharm. Chim. [5] 27, 300).

BUBULIN (from *βούς*, ox). The name of a peculiar substance, said by Morin to exist in cow-dung, and to be precipitated by metallic salts, tincture of galls, and alum, and therefore to be active in the application of cow-dung to calico-printing.

BUCHU *v.* OILS, ESSENTIAL.

BUCHU or BUCCO. The leaves of three varieties of *Barosma* (ord. Rutaceæ), viz. *B. betulina* (Bartl et Wendl. f.), *B. crenulata* (Hook.), and *B. serratifolia* (Willd.), are known under this name. The leaves are used medicinally by the South African natives.

Their composition has been studied by Brandes (Arch. d. N. Apoth. Ver. 22, 229), Landerer (Buchner's Répert. 84, 63), Flückiger (Pharm. J. 3, 4, 689; [3] 11, 219), Wayne (*ibid.* 3, 6, 723). By extracting the leaves with light petroleum, Bialobrzeski (Chem. Zentr. 1896, ii. 551) obtained chlorophyll, a resin, and an ethereal oil containing chiefly diosphenol, together with a terpene $C_{10}H_{18}$, b.p. 174°–176°, and a ketone isomeric with menthone, and having the constitution $C_{10}H_{18}O$, b.p. 206°–209°; it yields an oxime and a tribrom derivative. After extraction with light petroleum, the leaves, on treatment with cold alcohol, yield 3 p.c. of a brownish-green bitter resin insoluble in benzene, and when the alcoholic extract is treated with sodium carbonate or by other methods diosmin is deposited, forming tasteless, odourless crystals, m.p. 244°.

Semmler and McKenzie (Ber. 1906, 1158) found that the round leaves of *Barosma betulina* yield about 2 p.c. of an oil which crystallises on standing at ordinary temperature; but the long leaves of *Barosma serratifolia* yield 1 p.c. of an oil which remains liquid under similar conditions.

According to Kondakoff and Bochtschiew (J. pr. Chem. 1901, 63, 49), the best oil of bucco or buchu leaves contains 10 p.c. of hydrocarbons, consisting of a variety of *d*-limonene and dipentene; 60 p.c. of a ketone $C_{10}H_{16}O$, $[\alpha]_D$, −16°6′, b.p. 208·5° – 209·5°, which, on reduction, yields a menthol not identical with the natural product; 20 p.c. of diosphenol; 5 p.c. of resin; and 5 p.c. of other constituents (Kondakoff, J. pr. Chem. 1896, 54, 433). After removing diosphenol from the oil of buchu leaves, Tschugaeff succeeded in obtaining xanthogenide derivatives of *d*-menthol from a fraction of the residue (J. Russ. Phys. Chem. Soc. 1910, 42, 714; Skovortsoff, *ibid.* ii. 55). Diosphenol or buchu camphor (Bialobrzeski, *l.c.*; Kondakoff, *l.c.*; Semmler and McKenzie, *l.c.*; Semmler, Chem. Zeit. 1906, 30, 1208; Kondakoff, Chem. Zentr. 1905, ii. 1252; Chem. Zeit. 1906, 1090, 1100) is optically inactive, has m.p. 82°, b.p. 109°–110°/10 mm., 232°/755 mm. Its composition is probably $C_{10}H_{16}O_2$. It is a phenolic aldehyde, yielding an oxime, m.p. 156° (Semmler and McKenzie 125°). With hydrochloric acid it yields thymol and a little carvacrol. With hydriodic acid it yields a hydrocarbon $C_{10}H_{20}$, b.p. 165°–168°/762 mm.; whilst with sodium in alcoholic solution it forms (1) a menthol; (2) a crystalline glycol $C_{10}H_{18}(OH)_2$ m.p., 92°; and (3) an isomeric glycol, b.p. 141·5°–145°/13 mm. With alcoholic potash, a hydroxy acid of the terpene series, m.p. 94°, is obtained. This acid has been synthesised, and is identical with the natural product. The dibromide $C_{10}H_{14}O_2Br_2$ and other derivatives of diosphenol have also been obtained.

BUCKTHORN (*Rhamnus cathartica* [Linn.]). This plant is a native of England; it grows to a height of from 15 to 20 feet; its flowers are greenish-coloured, and its berries four-seeded. The juice of these when in an unripe state has the colour of saffron; when ripe and mixed with alum, it forms the sap or bladder-green of the painters (*v.* PIGMENTS); and in a very ripe state the berries afford a purple colour. The bark also yields a fine yellow dye.

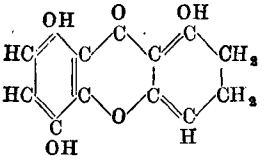
The berries of the *Rhamnus carthartica* (also known as Hungarian berries) have been examined by Tschirch and Polacco (Arch. Pharm. 1900, 238, 409), and evidently contain substances chemically distinct from those which are present in Persian berries.

Ether extracts from an aqueous extract of the berries *rhamnocitrin*, *rhamnolutin*, *rhamnochrysin*, and the residual watery liquid on boiling with dilute sulphuric acid gives, in addition to rhamnocitrin, *β-rhamnocitrin*. The berries already extracted with water contain *rhamnoemodin* and *rhamnonigrin*.

Rhamnocitrin $C_{12}H_{10}O_5$, yellow needles, melts at 221°–222°, and is soluble in alkaline solutions, with a yellow colour. Alcoholic lead acetate gives an organic coloured precipitate, and ferric chloride a green colouration. The solution in sulphuric acid possesses an intense green fluorescence.

Triacetylrhamnocitrin $C_{12}H_7O_5(C_2H_3O)_3$ forms colourless needles, melting at 199°–200°.

Rhamnocitrin appears to be a *dihydrotrihydroxyxanthone*, and probably possesses the following constitution :—



It dyes with iron mordant a green-brown, and with aluminium mordant a bright-yellow colour.

Rhamnolutin $C_{15}H_{10}O_6$, small canary-yellow needles, melts above 260°, and gives with lead acetate an orange-red precipitate, with ferric chloride a green-black colouration. Its sulphuric acid solution posseses a strong green fluorescence. *Tetraacetylrhamnolutin* $C_{15}H_6O_6(C_2H_3O)_4$, colourless needles, melts at 182°–183°.

Rhamnolutin dyes aluminium- and iron-mordanted fabrics respectively canary-yellow and green-brown shades. It appears to be a *tetrahydroxyflavone*, isomeric with luteolin and fisetin.

β-Rhamnocitrin $C_{13}H_{10}O_5$ is sparingly soluble in alcohol and acetic acid, but is distinct from rhamnetin ($C_{12}H_{10}O_5$?), and does not contain methoxy- groups. It melts above 260°, and, generally speaking, its reactions are the same as those of rhamnocitrin itself, but, on the other hand, it possesses stronger dyeing property. *Diacetyl-β-rhamnocitrin* $C_{13}H_8O_5(C_2H_3O)_2$ forms colourless needles melting at 190°–191°.

β-Rhamnocitrin, according to Tschirch and Polacco, appears to resemble very closely the β-rhamnetrin of Schutzenberger (*see* PERSIAN BERRIES).

Rhamnoemodin $C_{15}H_{10}O_5$, m.p. 254°–255°, is similar to *frangula emodin* (*R. frangula*) which, according to Oesterle, melts at 250°.

Rhamnonigrin is converted by boiling with nitric acid into *chrysamminic acid*, and by digestion with boiling alcoholic potash into *emodin*.

The **alder buckthorn** (*Rhamnus frangula*) grows naturally, and is very abundant in woods and thickets, in some parts of Britain. The berries of this species are often substituted for those of the above ; but they are easily detected, since they contain only two seeds. In a green state they dye wool green and yellow ; when ripe, bluish-grey, blue, and green. The bark also dyes yellow, and, with preparation of iron, black (Lawson)

Rock buckthorn (*Rhamnus saxatilis*), yields berries which are used to dye morocco leather yellow. These, in common with the narrow-leaved buckthorn berries (*R. alaternus* [Linn.]) and those of the yellow-berried buckthorn (*R. infectorius* [Linn.]), are sold as Avignon berries. The wood of the *Rhamnus erythroxylon* (which is a native of Siberia, but grows freely in this climate), in a ground state yields the bright-red colour known to dyers under the name of *redwood*. A. G. P.

BUCK WHEAT (*Fagopyrum esculentum* [Moench.]) is grown mainly for poultry and also for pig- and cow-feeding in Europe. Its flowers furnish excellent pasturage for bees. Kellner gives the following analyses :—

—	Water	Protein	Fat	Carbo-hydrates	Fibre	Ash
Seed	14·1	11·3	2·6	54·8	14·4	2·8
Fine meal	14·7	8·6	1·9	72·6	0·8	1·4
Coarse meal	12·0	31·8	8·4	38·3	4·8	4·7
Fine bran	12·0	15·2	4·5	50·0	11·3	7·0
Coarse bran	15·6	8·0	1·8	34·2	37·6	2·8
Husks	13·2	4·6	1·1	35·4	43·5	2·2
Straw	16·0	4·8	1·2	34·6	38·2	5·2
Whole plant, in flower	83·7	2·5	0·6	7·8	4·3	1·1
„ „ hay	14·0	10·5	2·1	35·6	31·4	6·4

Buckwheat, after soaking in water, furnishes excellent food for cattle and pigs, though not very suitable for young animals.

The starch of buckwheat occurs in rounded angular grains of small size, showing a distinct hilum and a tendency to agglomerate.

The flour is largely used in making buckwheat cakes, popular in America, but rarely met with in England. H. I.

BUCURUMANGA RESIN. A fossil resin, occurring in an auriferous alluvium near Bucurumanga, New Granada. It is light-yellow, transparent, somewhat heavier than water, becomes strongly electric by friction ; is insoluble in alcohol ; swells up in ether, becoming opaque ; melts when heated ; burns in the air without residue. It resembles amber in outward appearance, but does not give succinic acid on dry distillation. It contains 82·7 p.c. C, 10·8 p.c. H, and 6·50 p.c. O (Boussingault, Ann. Chim. Phys. [3] 6, 507) (*v.* RESINS).

BUFFALO RUBIN *v.* AZO- COLOURING MATTERS.

BUHRSTONE or **BURRSTONE.** A hard, tough rock consisting of chalcedonic silica with a cellular texture, especially suitable for use as millstones for grinding corn, paints, &c. It is white, grey, or creamy in colour. The best stones are from the Tertiary strata of the Paris basin, and have originated by the silification of fresh-water limestones, the cellular spaces representing the casts of fossil shells and *Chara* seeds. L. J. S.

BUNTKUPFERERZ (Ger.). Variegated copper ore. This term is commonly applied, even by English mineralogists, to an ore of copper otherwise known as *Bornite* (*q.v.*), *Erubescite*, *Phillipsite*, and *Purple Copper Ore*. Called ' horse-flesh ore ' by the Cornish miners.

BURGUNDY PITCH or **NORWAY SPRUCE RESIN.** (*Fichtentarr*, *Tannenharz*, Ger. ; *Poix des Vosges*, *Poix blanche*, *Poix jaune*, *Barras*,

Fr.) The resin of *Picea excelsa* (Link.) purified by melting in hot water and straining. It is an opaque, yellowish-brown, hard, brittle resin; its taste is sweet and aromatic. It is very soluble in glacial acetic acid, acetone, and alcohol. Used in making plasters. It is much adulterated. The substance usually sold by this name in England is made by melting colophony with palm-oil or some other fat, and stirring in water to make the mixture opaque (Morel, Pharm. J. [3] 8, 342) (*v.* RESINS).

BURNETT'S FLUID. A solution of zinc chloride is commonly known as Sir William Burnett's disinfecting fluid. It is used as a disinfectant and as a preservative of constructional timber.

BURTON WATER CRYSTALS contain, according to Moritz and Hartley, 31·8 CaO, 40·4 SO_3, 1·04 Cl, 5·46 MgO, and 21·19 OH_2 (J. Soc. Chem. Ind. 2, 82).

BUSSORAH GUM *v.* GUMS.

BUTALANINE *v.* VALINE.

BUTANE *v.* BUTYL- COMPOUNDS.

BUTANONE (*Methylethylketone*) *v.* KETONES.

BUTEA FRONDOSA. The *Butea frondosa*, also called *Dhak* or *Pulas*, is a fine tree, 30–40 feet high, belonging to the order *Leguminosæ*. It is common throughout India and Burma, and is found in the North-West Himalaya, as far as the Jhelum River. The flowers, which in the dried condition, are known as tísu, késú, kesuda or palás-képpúl, have a bright orange colour, and, although they are much larger, closely resemble in appearance the common gorse-flower (*Ulex europæus*), with which, indeed, they are botanically allied. Large quantities of the flowers are collected in March and April, and employed by the natives to produce a yellow dye, much used during the Holi festival. The dyeing operation, which consists in steeping the material in a hot or cold decoction of the flowers, is virtually a process of staining, because the colour can be readily washed out. On the other hand, a more permanent result is sometimes produced either by first preparing the cloth with alum and wood ash or by adding these substances to the dye-bath.

From the *Butea frondosa* is also obtained the so-called 'Butea gum' or 'Bengal kino,' employed by the natives for tanning leather, and the tree is of additional interest because in many parts of India the lac insect (*Coccus lacca*) is reared upon it. This, as is well known, causes the formation of stick lac, from which shellac and lac dye are prepared.

Butin $C_{15}H_{12}O_5$. The flowers are extracted with water, and the extract digested at the boil with a little sulphuric acid. A light viscous precipitate devoid of dyeing property separates, and this is removed while hot and the filtrate left overnight. The clear liquid is now decanted from a small quantity of tarry substance, and partially evaporated on the water-bath. A further quantity of a black viscous precipitate thus separates, and when this has been removed the filtrate, after some days, deposits crystals of the colouring principle. For purification the product is dissolved in a little alcohol, the mixture poured into ether, and the solution well washed with water. The liquid is evaporated, and the residue repeatedly crystallised from dilute alcohol.

Butin crystallises from alcohol in colourless needles with $\frac{1}{2}H_2O$, m.p. 224°–226°, and from water in pale-yellow needles with $2H_2O$; dissolves in alkaline solutions with a pale orange-red tint, and gives with alcoholic acetate of lead a faintly yellow almost colourless precipitate. It forms a *triacetyl* derivative $C_{15}H_9O_5(C_2H_3O)_3$ colourless leaflets, m.p. 123°–125°, and a *tribenzoyl* compound $C_{15}H_9O_5(C_7H_5O)_3$, colourless needles, m.p. 155°–157°. On fusion with alkali at 200°–220° butin gives *protocatechuic acid* and *resorcinol*.

When butin is boiled with dilute potassium hydroxide solution, the pale-coloured liquid becomes much darker, and on acidifying an orange crystalline precipitate separates which consists of butein.

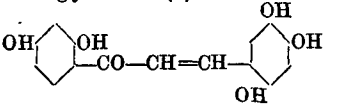
Butein $C_{15}H_{12}O_5,H_2O$, needles, melts at 213°–215°; dissolves in alkaline solutions with a deep orange-red colour, and with alcoholic lead acetate gives a deep-red precipitate. *Acetyl butein* $C_{15}H_8O_5(C_2H_3O)_4$, pale-yellow needles, melts at 129°–131°.

When fused with alkalis butein gives *resorcinol* and *protocatechuic* acid, whereas by the action of boiling 50 p.c. potassium hydroxide solution, *protocatechuic* acid and *resacetophenone* are produced.

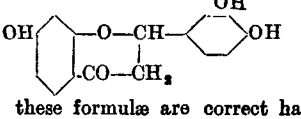
By methylation with methyl iodide butin gives *butintrimethylether* $C_{15}H_9O_2(OCH_3)_3$, colourless plates, m.p. 119°–121°, and also *buteintrimethylether* $C_{15}H_9O_2(OCH_3)_3$, yellow leaflets, m.p. 156°–158°. In a similar manner, butein yields not only buteintrimethylether, but also butintrimethylether.

The constitution assigned to butein is that of a *tetrahydroxybenzylidene acetophenone* (*tetrahydroxychalkone*) (1), and to butin that of the corresponding *flavanone* (2):

(1)

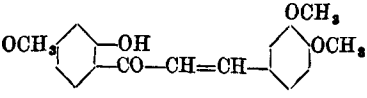


(2)

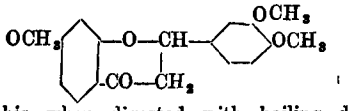


and that these formulæ are correct has been established by the synthesis of butein and butintrimethylethers. Thus by the condensation of resacetophenonemonomethylether with veratricaldehyde, buteïntrimethylether (I) is produced:

I.



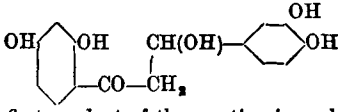
II.



and this, when digested with boiling dilute alcoholic sulphuric acid, a method devised by Kostanecki and his colleagues (Ber. 1904, 37, 784, 773, 779), gives butintrimethylether (II).

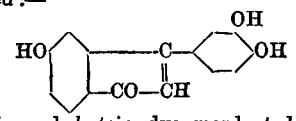
Butein itself is also converted into butin by means of dilute alcoholic sulphuric acid, and the butin can again be transformed into butein by the action of potassium hydroxide solution. With alcoholic potash butintrimethylether also

gives buteintrimethylether, and these changes are readily explained if it is assumed that the intermediate compound or its trimethyl ether



is the first product of the reaction in each case, and that this subsequently, by loss of water, passes into either chalkone or flavanone, or both.

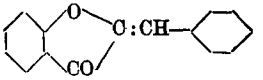
When butein dissolved in acetic acid is treated with a few drops of sulphuric acid, and the solution is boiled, a new substance gradually separates in the form of crystals, which possess a beetle-green iridescence, and dissolves in alkaline solutions with a deep-blue colour. The acid liquid decanted from the crystals, on dilution with water, gives a brown precipitate soluble in alkalis with a bluish-violet colouration, which dyes mordanted calico shades of a similar character to those yielded by anthragallol. It appears likely that this more soluble substance represents the first product of the reaction, and is subsequently converted into the green iridescent compound. A consideration of the formula of butein renders it unlikely that these new substances are anthraquinone derivatives; on the other hand, it is suspected that the formation of a ring takes place, and that an indone derivative of the following type is first produced :—



Butin and butein dye mordanted woollen cloth identical shades, though as butin gives with an alcoholic lead acetate a practically colourless precipitate, it is not to be regarded as a colouring matter. In other words, butin is merely a colouring principle, and is converted during the dyeing operation by the action of the mordant into the colouring matter butein. The following shades are obtained :—

Chromium	*Aluminium*	*Tin*	*Iron*
Reddish-brown	Brick red	Full yellow	Brownish black

and these are strikingly similar to those yielded by some of the phenylketocumaran colouring matters artificially prepared by Friedländer and Rudt (Ber. 1896, 29, 879).



The Butea flowers contain but a trace of free butin or butein, and the glucoside present, and which has not yet been isolated, is probably that of butin. This glucoside does not decompose readily during the dyeing process, hence the flowers do not dye mordanted cotton. In wool-dyeing, where acid-baths are employed, a better result is obtained, although in this case the shades possess but little strength. If the glucoside is first hydrolysed by boiling the flowers with dilute hydrochloric acid, or if sulphuric acid is employed, and the acid then neutralised with sodium carbonate, a material is obtained which readily dyes by the usual methods. Such products give the following shades: with chromium, deep terracotta; with aluminium, a bright orange; with tin, bright yellow; and with iron, a brownish-olive. The chromium colour is characteristic, and is much redder in tint than that yielded by any known natural yellow dye. A. G. P.

BUTEA GUM. The juice of *Butea frondosa* (Roxb.), often sent into the market instead of genuine kino. It forms black-brown, slightly lustrous, brittle lumps, has an astringent taste, and yields pyrocatechin by dry distillation.

BUTTER. Butter is the fatty product prepared from the milk of the cow. When similar substances are obtained from the milk of other mammals, their origin is indicated in the description, *e.g.* goats' butter, buffalo butter. Fatty food substances of vegetable origin and similar to butter in consistency are also sometimes described as butter, but with a prefix, as *vegetable butter, cocoa-nut butter.*

Butter consists of milk- or butter-fat, with water, and small quantities of milk proteins, lactose, mineral salts, and natural colouring matter. The proteins and lactose, together with the mineral matter associated therewith, are spoken of collectively as *curd.* Commercial butter may also contain common salt, preservatives, and colouring matter, added during manufacture. The added salt and preservatives are not included with the curd in giving the composition of butter, but are separately estimated.

Fat exists in milk in the form of minute globules in a state of suspension in the milk serum. In the process of churning, the fat globules coalesce, producing irregularly-shaped granules of butter. These are strained from the serum, or buttermilk, washed with water, and worked into a mass on a table by means of mechanical rollers, or, as in older processes, by hand. Salt, preservatives, colouring matter, are added, if desired, after washing the butter granules with water.

Milk may be directly churned for the purpose of obtaining butter, and, in some remote districts, this process is still followed. It is, however, usual to churn *cream,* that is, the fatty layer which rises to the surface on allowing milk to stand or on subjecting it to centrifugal action.

Cream may be churned in a fresh condition before souring has taken place. In such a case, the period of churning is longer, and the operation must be carried out at a lower temperature than when ripened cream or milk is employed. It is therefore usual to churn ripened cream. The ripening may be effected by standing the cream, and is accelerated by the addition of a little buttermilk or pure culture starters containing suitable bacteria.

Various views are held as to what takes place during the operation of churning. Fleischmann (Book of the Diary, 159) states that 'the milk-fat is converted from fluid to solid condition by the shaking which it undergoes,' that is, that churning results in the solidification of fat which in milk is in a superfused condition. On the other hand, Richmond's results (Dairy Chemistry, Ap. 339) would indicate that the fat before churning may be in a solid condition. Whether fat as present in milk is surrounded with some form of membrane (Béchamp, Storch) or with a thin watery covering (Fleischmann),

the mechanical operation of churning appears to rub away or remove the protective coating, and thus enable the milk globules to coalesce, forming butter. As to the theories regarding the structure of the fat globules in milk, *see* papers by Storch (Analyst, 1897, 22, 197), Beau (Revue Générale du Lait, 2, 15, 1903), and Richmond (Analyst, 1904, 29, 185).

The quantity of water remaining in finished butter is governed by the conditions of manufacture. Churning at too high a temperature renders the removal of excess water during working difficult. It results in over-worked or 'greasy' butter; or butter with an excessive quantity of water. The maximum limit permissible in England for water in butter is 16 p.c. Canada, Queensland, Holland, have the same limit. Victoria has 15 p.c.; Germany, 16 p.c. for salted, and 18 p.c. for unsalted; and Belgium, 16 p.c.

The proportion of curd may vary from 0·2 to 2·0 p.c. according to method of manufacture, lower quantities being present where freshly separated cream is churned than in the case of ripened cream. Well-made butter rarely contains so high a quantity as 2 p.c., and where this quantity is found, examination should be made for the presence of added non-fatty milk solids. No limits have been fixed as to the non-fatty milk solids permissible in butter, but the Butter and Margarine Act, 1907, gives power to the Board of Agriculture and Fisheries to make regulations on the point.

Van Slyke and Hart (J. Amer. Chem. Soc. 1905, 27) state that when 0·5 p.c. or over of lactic acid is in the cream, the casein is present in the butter as casein lactate, but in butter made from sweet cream as calcium casein. They also make suggestions with regard to the relation between casein compounds and mottled butter. Richmond (Analyst, 1906, 31, 178) has found the average amount of casein to be 0·38 p.c., and not to exceed 0·5 p.c.

The mineral matter in butter (to which no foreign substance has been added during manufacture) consists of the inorganic substances derived from the buttermilk enclosed within the butter granules, and from the caseous matter adhering to the fat. It is really the ash of the curd, or the non-fatty milk solids of the butter.

When butter is heated, the fat melts and separates from the aqueous, curdy portion. After allowing this to settle, the fatty layer is filtered through a warm funnel, and the fat obtained as a clear oil, usually of a yellow colour, but under certain conditions almost colourless, setting to a granular crystalline mass. The fat so obtained consists of glycerides of fatty acids together with the natural or added colouring matter, if any, of the butter, and some unsaponifiable substances, *e.g.* cholesterol, associated with the natural fat. The total quantity of the unsaponifiable matter does not exceed 0·4 p.c. (Bömer, Zeitsch. Nahr. Genussm. 1901, 4, 1070).

The glycerides of butter-fat contain butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic acids, as triglycerides, with a possibly small quantity of mono- and diglycerides. Bell has shown the presence of 'mixed' glycerides, and describes (Chemistry of Foods, 45) an oleopalmitobutyrate. Browne (J. Amer. Chem. Soc. 1899, 613) finds 1·0 p.c. of dihydroxystearic acid; but Lewkowitsch throws doubt upon the presence of any hydroxy acids (Oils and Fats, 4th ed. ii. 667). The composition, as given by Bell (Chem. of Foods, 48), is compared with that given by Browne (J. Amer. Chem. Soc. 1899, 21, 807).

100 parts of fat on saponification yield:

	Bell	Browne	
Butyric acid . .	6·13	5·45	
Caproic ,, . .	2·09	2·09	2·90
Caprylic ,, . .		0·49	
Capric ,, . .		0·32	
Lauric ,, . .	—	2·57	
Myristic ,, . .	49·46	9·89	50·33
Palmitic ,, . .		38·61	
Stearic ,, . .		1·83	
Oleic ,, . .	36·10	32·50	
Dihydroxy stearic acid	—	1·00	

Caldwell and Hurtley (Chem. Soc. Trans. 1909, 95, 853) have fractionally distilled samples of butter fat in the vacuum of the cathode light, and determined certain values of the distillates. They conclude that there is no tributyrin in butter-fat, and probably no triolein, the oleic acid being distributed among the glycerides present, most of it as oleostearopalmitin. Caldwell and Hurtley (*l.c.*) have also similarly distilled the fatty acids.

The most characteristic feature of butter-fat is the presence of fatty acids soluble in water and volatile in steam; and the earliest work on butter was directed to the estimation, directly or indirectly, of butyric acid, the largest constituent of the soluble or volatile portion.

Hehner and Angell (Butter: its Analysis and Adulterations, Churchill, 2nd ed. 1877), following the suggestion of Chevreul, proposed in 1874 to obtain the butyric acid by distillation of the acids liberated by dilute sulphuric acid after saponification of the fat with alkali. In consequence of the variation in the results, they proposed the determination of the acids insoluble in water, Dupré subsequently adding in the same process the titration of the water-soluble acids (Analyst, 1876). The quantity of insoluble fatty acids is frequently spoken of as the 'Hehner value.' The process consists in saponifying a weighed quantity of the fat with alcoholic potash, liberating the fatty acids from the aqueous, alcohol-free, soap solution with excess of dilute sulphuric acid, filtering and washing with hot water the insoluble acids, finally weighing these, and titrating the dissolved acids. The quantity of soluble acids usually falls between 4·2 and 6·0 p.c. (calculated as butyric acid), and the weight of the insoluble acids between 90 and 87·5 p.c.

Reichert adopted a modification of Chevreul and Hehner's distillation of the butyric acid, operating with a definite quantity of fat under prescribed conditions, and thus avoiding the necessity of the distillation of the whole of the volatile acids. Reichert took 2·5 grams of fat; and the number of cubic centimetres of decinormal alkali required to neutralise the distillate from this quantity, operating as described, was the original Reichert number (Chem. Soc. Trans. 1879, A, 406; Zeitsch. anal. Chem. 1879, 18, 68). Meissl suggested the use of 5 grams of fat (Chem. Soc. 1880, A, 828), and Wollny added a number of modifications (Chem. Soc. 1888,

A, 200). This process was adopted by a committee consisting of the Principal of the Government Laboratory and the members of the Society of Public Analysts, as the method to be used in the estimation of butter-fat in margarine (Analyst, 1900, 25, 309). The conditions of distillation must be strictly observed, as the whole of the volatile acid is not distilled during the experiment. Richmond (*ibid.* 1895, 20, 218) found only 87 p.c. of the total volatile acids in the distillate. Jensen's results confirm this (Zeitsch. Nahr. Genussm. 1905, 272). Leffmann and Beam used soda dissolved in glycerol for the saponification (Analyst, 1891, 16, 153). The details of the process, as adopted by the committee, are: 5 grams of clear, melted fat are weighed into a flask of a capacity of 300 c.c., and saponified with 2 c.c. of soda (prepared by dissolving sodium hydroxide in equal weight of water), and 10 c.c. of alcohol, by heating on a hot water-bath under reflux condenser for 15 minutes. After evaporation of the alcohol, the dry soap is dissolved in 100 c.c. of hot water, 40 c.c. of normal sulphuric acid and a few fragments of pumice are added, and the flask connected with a condenser. It is then heated so that 110 c.c. of distillate are collected in about 30 minutes. The distillate is shaken, 100 c.c. filtered off, and titrated with decinormal alkali, using phenolphthalein as indicator. (Further details as to size of flask, tubes, still-head, condenser, will be found in the Analyst, 1900, 25, 309.) The number of cubic centimetres of decinormal alkali required for neutralisation, when multiplied by 1·1 and corrected to 5 grams, is the 'Reichert-Wollny number.'

The proportion of volatile acids in butter-fat varies. In the late autumn season, in the case of cows fed in the open, the butter-fat contains less butyric acid than it does during the spring and summer. Towards the close of the lactation period, butter fat also shows a depreciation in the amount of volatile acids. Among other factors affecting the character of the fat are the nature of the food, and the sensitiveness of the cows to varying climatic conditions and their surroundings. Hence the uncertainty as regards the limits that should be adopted. In the case of butter made from the milk of mixed herds, when the influence of individual cases does not seriously depreciate the butter from the whole herd, the proportion of volatile acids under ordinary conditions of feeding and housing reaches a maximum in April–May–June, and is at a minimum in October–November. Lewkowitsch has collected a number of results representing the produce of different countries (Oils and Fats, 4th ed. ii. 686). Although the milk from individual cows or small herds may, in consequence of special circumstances, occasionally yield butter-fat giving a Reichert-Wollny number below 24, the butter from the mixed milk of herds under normal conditions usually has a Reichert-Wollny number falling between 24 and 32. The Committee on Butter Regulations appointed by the Board of Agriculture in this country recommended that the figure 24, arrived at by the Reichert-Wollny method, should be the limit below which a presumption should be raised that butter is not genuine (Com. on Butter Regns. Report, Cd. 1749, 18). France has fixed a minimum limit of 24; Germany, of 25; Sweden, of 23; the United States, of 24; Italy declares butter with a Reichert-Wollny number below 20 adulterated, between 20 and 26 suspicious, above 26 pure; Belgium declares butter to be abnormal, and its sale is prohibited, if the Reichert-Wollny number falls below 28, and if in addition the fat has a Zeiss number above 44 at 40°, a sp.gr. below 0·865 at 100°, a saponification value below 222, and a Hehner number above 88·5.

Handby Ball (Analyst, 1907, 32, 202) gives results of butters produced in Ireland, and shows that during the months of December and January, when the output of milk is lowest, the Reichert-Wollny number frequently falls below 24. The lowest numbers occur when the milk is derived from cows at the end of the lactation period.

Brownlee (Jour. Dept. Agric. for Ireland, 1910, 10, 438) has published results of analyses of Irish butter produced in 1908–9. He found 16·2 p.c. of samples below 24, 11·4 p.c. below 23, 5·5 p.c. below 22, and 1·4 p.c. below 21. The tables given by Brownlee show that throughout the year the Reichert-Wollny number varies in each case with the percentage output of butter from the particular dairy, and the results confirm the opinion that the chief factor influencing the Reichert-Wollny number is the lactation period of the cows supplying the milk.

The conclusion that butter is genuine because the Reichert-Wollny exceeds 24, may be erroneous, as this number may have been the result of mixing genuine butter having a high Reichert-Wollny number with some other fat. On the other hand, butter falling below 24 may be genuine but abnormal. In order to be in a position to establish the genuineness of butter, the Netherlands Government has organised a system of butter control, by means of which the associated creameries are frequently inspected and the butter produced regularly analysed. Consignments from the factories bear a government label, giving particulars of origin, so that the officials can trace the butter and ascertain the Reichert-Wollny number of the butter produced at the creamery.

Higher homologues of butyric acid volatilised in the steam during the Reichert process do not wholly dissolve in the distillate, and the determination of the insoluble portion affords another index to the character of the fat, as will be seen later.

Butter-fat has a sp.gr. at 37·8°/37·8° of 0·910-0·913 (Thorpe, Chem. Soc. Trans. 1904, 249). The individual data in Bell's results range from 0·9094 to 0·9139, but he states the ordinary range is 0·911 to 0·913. The sp.gr. is affected by prolonged heating of the fat and also by the storage of the fat for a lengthened period.

The reading with the Zeiss butyro-refractometer at 45° falls usually between 38 and 42. In 371 samples of genuine butter examined, the range was 37 to 45 (Com. on Butter Regns., Ap. 585). Excluding 14 exceptional butters, the average range was 39·4 to 42·0 (Chem. Soc. Trans. 1904, 249). (Zeiss readings are taken at various temperatures by different observers. To convert the scale divisions observed at a lower temperature into the scale divisions at a higher temperature, deduct 0·55 of a division for each degree of temperature that the reading has been taken below the required temperature;

conversely, add 0·55 of a division for each degree of temperature that the reading has been taken above the required temperature).

The saponification value of the fat was suggested by Koëtstorffer (Frdl. 1879, 199), and is frequently known as the Koëtstorffer number. It is the quantity of potash expressed in milligrams required to saponify 1 gram of fat. The glycerides in butter-fat contain acids of comparatively low molecular weights; in consequence, the quantity of potash for saponification will be relatively high when compared with fats in which the glycerides contain only acids of high molecular-weight, as in animal fats in general. Butter-fat gives figures on the average between 219·9 and 232·5 (Thorpe). Koëtstorffer gave 227 as a mean figure. This value bears a close relationship to the Reichert number.

The iodine value varies considerably, falling between 26·0 and 35·0 (Hübl), 29·0 and 43·0 (Jensen), and 26·0 and 38·0 (Wollny).

The various data show their dependence upon one another, within certain limits, when a comparison is made. This parallelism is shown in the following table (Thorpe, Chem. Soc. Trans. 1904, 254):—

No. of sample	R.W. number	Specific gravity at 37·8°	Saponification value	Zeiss at 45°	Soluble acids, p.c. on fat	Insoluble acids, p.c. on fat	Mean molecular weight of insoluble acids
7	22·5	0·9101	219·9	42·0	4·3	90·1	266·9
17	23·5	0·9104	221·3	41·5	4·5	89·7	265·5
15	24·5	0·9108	223·3	41·5	4·7	89·4	265·0
27	25·5	0·9110	223·4	41·3	4·8	89·3	264·2
37	26·5	0·9113	225·3	41·0	4·9	88·9	261·9
51	27·5	0·9114	226·7	40·6	5·2	88·7	261·7
78	28·5	0·9118	228·3	40·1	5·4	88·4	260·9
56	29·5	0·9120	229·9	40·1	5·6	88·3	259·6
41	30·5	0·9123	231·4	39·9	5·8	87·9	260·1
18	31·3	0·9125	232·2	39·7	5·7	87·9	258·0
10	32·6	0·9130	232·5	39·4	6·0	87·7	257·8
357							

The examination of butter comprises: (1) the determination of water, fat, curd, salt; (2) examination of the fat; (3) examination of the butter for preservatives, colouring matter, and substances foreign to butter.

1. Water. The sample for examination should be not less than 50 grams, and should be placed in a bottle and closed securely with screw-cap or stopper. The bottle is then heated at a temperature of about 50° until the butter-fat has melted, when it is vigorously shaken to emulsify the fat and water. The shaking is continued while the bottle and contents cool, until the butter is of the consistency of thick cream. From 6 to 8 grams are then weighed into a flat-bottomed dish, in which is a glass rod with flattened end. The dish is heated on a steam-bath for an hour with frequent stirring of the butter, after which it is cooled and weighed. It is again heated until the weight is constant. The operation is considerably accelerated by using aluminium dishes, heated on an aluminium hot plate adjusted to a temperature of 100° to 105°.

Other methods are Henzold's (in which pumice is mixed with the butter) and Wibel's (J. Soc. Chem. Ind. 1893, 630).

Fat. The butter from which the moisture has been evaporated is extracted with ether, filtered from curd and salt, and, after evaporation of the solvent, is dried and weighed, or the matter insoluble in ether is weighed, and the fat taken by difference. The Governments of Queensland, Victoria, and Germany have fixed a minimum limit for fat of 80 p.c.; Italy, of 82 p.c.; and the United States, of 82·5 p.c.

Curd. In the case of butters free from salt and preservative, the curd is the matter not soluble in ether or other solvent. The separate determination of the proteins and lactose must be carried out to decide whether a butter contains added non-fatty milk products. 15–20 grams of butter are weighed in a dish and dried on the water-bath with frequent stirring. The fat is extracted with ether, and the ether-insoluble matter transferred with concentrated sulphuric acid to a Kjeldahl digestion flask, adding the filter paper used for filtration. The quantity of nitrogen multiplied by 6·38 gives the proteins. Richmond gives 6·39 (Analyst, 1908, 33, 180).

The lactose is taken by difference, after deducting from the total curd the proteins and inorganic salts. But it is in all cases preferable to make a direct determination, and this becomes necessary when boric acid is present. The lactose and proteins may then be estimated as follows: The residue from extraction with ether of 20 grams of butter is mixed with about 40 c.c. of water, made just acid with acetic acid, and the proteins precipitated by adding a few drops, being careful to avoid excess, of Fehling's copper sulphate solution. It is then filtered on tared paper, washed, dried at 100°, weighed, and incinerated. The weight less the ash is the proteins. The filtrate is made up to 100 c.c. and an aliquot portion taken for gravimetric lactose determination. Where sugar only is required, the residue from ether extraction may be washed into 100 c.c. flask, cleared with copper sulphate, made up to 100 c.c., and an aliquot portion filtered. The quantity of lactose should not exceed 0·4 p.c., and is usually much less.

The matter insoluble in ether contains, in addition to the true curd and other non-fatty solids of milk, common salt, borax, a portion of the boric acid (partly in solution in ether), and certain other preservatives, if these have been added to the butter. The common salt is estimated by extracting the weighed quantity of curd in the total curd determination with hot water, and titrating the solution with standard silver nitrate.

2. Examination of the fat. The examination of the fat to ascertain its purity is one of considerable difficulty, since butter adulteration has been directed to the admixture of fats prepared so as to give no distinctive reaction. All animal fats, such as refined lard and beef fat, and many vegetable fats used for this purpose, have practically no volatile acids. Hence the addition to butter of fats of this class reduces the soluble volatile acids number. Other vegetable fats contain volatile acids only partially soluble in water. To this class belong cocoa-nut oil and palm-kernel oil.

Vegetable fats, unless specially prepared, contain phytosterol, and the detection of this substance establishes the presence of foreign fat. Other fats, as cotton seed and sesamé, give specific reactions, and may therefore be directly tested for. It has, however, been established that the constituent giving the reaction may be communicated to a slight extent to milk and thence to butter through feeding the animals with oil-cakes made from these seeds. Positive reactions in these cases must therefore be supported by other evidence. With the object of detecting the addition of foreign fat, it is enacted in some countries that margarine and margarine fats must contain, when prepared for sale, a small quantity of sesamé oil, as a tell-tale substance when butter with which such fat has been mixed is examined.

(*a*) The soluble volatile acids are estimated by the Reichert-Wollny process described above.

Reychler (Bull. Soc. chim. 1901, 25, 142) proposed the extension of the Reichert-Wollny process to include the estimation of the volatile insoluble acids. Wauters (Analyst, 1901, 26, 128) modified the Reichert process and made two distillations, determining the values for both soluble and insoluble volatile acids.

Polenske (Zeitsch. Nahr. Genussm. 1904, 273) adopts the Reichert-Wollny process and estimates in the same operation the soluble and insoluble volatile acids. 5 grams of the fat are weighed into a 300 c.c. flask and saponified with 2 c.c. of soda solution and 20 grams of glycerol by heating the flask over the free flame. The flask is cooled below 100°, and 90 c.c. of hot water and a little powdered pumice are added. When the soap is in solution the fatty acids are liberated with 50 c.c. of sulphuric acid (25 c.c. pure H_2SO_4 in one litre), the flask attached at once to a condenser arranged vertically, and heated so that 110 c.c. of distillate are collected in about 20 minutes. The heating is then stopped, and the receiving flask replaced by a measuring jar to catch the drainings of the condenser. The distillate is cooled to 15°, gently shaken, and 100 c.c. filtered off and titrated with decinormal soda. The number of cubic centimetres (multiplied by 1·1 and corrected to 5 grams) is the Reichert-Wollny number. The remainder of the distillate is poured on the filter paper, and then washed with three quantities, of 15 c.c. each, of water, each of which has been passed in succession through the condenser tube, the measuring jar, and the 110 c.c. flask. These washings are rejected. The 110 c.c. flask is then placed under the filter funnel, and the water-insoluble acids dissolved in alcohol by passing three quantities, of 15 c.c. each, of neutral alcohol, successively through the condenser tube, measuring jar, and filter paper. The alcoholic filtrates are titrated with 1/10 normal soda, using phenolphthaleïn as indicator. The number of cubic centimetres required is the insoluble volatile acids number.

In butter-fat this number varies with the soluble acids number. Polenske (*l.c.*) gave a range of 1·35 insoluble for 20·0 of soluble, to 3·0 insoluble for 30 of soluble. Individual butters may, however, give numbers outside this range. Rideal and Harrison (Analyst, 1906, 31, 254) give results of examination of a number of English butters. Harris (*ibid.* 1906, 31, 353) shows the variation in insoluble acids number for the same soluble acids number. Hesse (Chem. Zentr. 1905, 1, 566) says the limits given by Polenske should be higher. Hesse and Harris (*l.c.*) point out the importance of following exact details of process, particularly in regard to size of pumice. Harris gives varying results obtained by operating with pumice of different sizes.

Cocoa-nut fat gives a soluble acids number by this process of 7–9 and an insoluble acids number of 15–18. Hence the addition of this fat to butter depresses the Reichert-Wollny number, and increases the insoluble volatile acids number. At the same time, the Zeiss and iodine numbers would be lowered, and the saponification value would be increased. Thus, while the Polenske value alone might not itself be sufficient evidence of adulteration in cases of small quantities of admixed cocoa-nut fat, the disturbance of the co-relation between the other numbers would establish the presence of the adulterant. Palm-kernel fat has a Reichert-Wollny number of 5, and insoluble volatile acid number of 10–12; other vegetable and animal fats have a total volatile acids number less than 1. The addition of palm-kernel oil would operate in a similar manner to that of cocoa-nut fat; animal fat would depress both the soluble and insoluble volatile acids, but the former to a greater extent than the latter. Thorp (Analyst, 1906, 31, 173) makes a second distillation in the ordinary Reichert process, after addition of more water, and obtains an increased value for the total insoluble volatile acids. He gives results of examination of butters and mixtures.

Muntz and Coudon (Mon. Sci. 1904, 18; Analyst, 1905, 30, 155) have devised a similar method for determining the ratio between the soluble and insoluble volatile acids. They saponify 10 grams of fat with hot strong aqueous potash, dissolve the soap in water, add phosphoric acid solution, and distil 200 c.c., using a spiral dephlegmator of considerable length. The distillate is filtered, and the soluble acids titrated. The insoluble acids in the condenser tube and flask, and on the paper are also dissolved in alcohol and titrated. They found that pure butters yielded from 4·79 to 6·01 p.c. of soluble volatile acids (as butyric acid) and 0·5 to 0·87 p.c. of insoluble; while cocoa-nut fat gave 1·15 to 1·27 p.c. soluble, and 3·01 to 3·63 p.c. insoluble. They determine the following ratios:

$$\frac{\text{insol. vol.}}{\text{sol. vol.}} \times 100 = 9{\cdot}1\text{–}15{\cdot}6$$

for genuine butter, and 250·3 to 282·3 for cocoa-nut fat.

Vandam (Analyst, 1901, 26, 320) determined the ratio between the total fatty acids soluble in 60 p.c. alcohol, and those soluble in the alcohol but insoluble in water. Robin (Compt. rend. 1906, 143) practically applies the same principle in his method. He found that the ratio $\frac{\text{insol.}}{\text{sol.}} \times 10$ was 8·3 to 12·7 butter, 232 for margarine, and 226 for cocoa-nut fat. Shrewsbury and Knapp (Analyst, 1910, 35, 385) remove the acids soluble in water, and then determine the solubility of the remaining fatty acids in dilute alcohol. They find a solubility figure of 28 for

butter and 163 for cocoa-nut fat. It has been shown (Caldwell and Hurtley, Analyst, 1909, 34, 274) that lauric and myristic acids are the chief constituents of cocoa-nut fatty acids, but that these acids are only present to a slight extent in butter; and these processes are therefore based upon the solubility in 60 p.c. alcohol and insolubility in water of these acids. Fendler (Zeitsch. Nahr. Genussm. 1910, 19, 544; Analyst, 1910, 35, 355) has a similar process.

Avé-Lallemant (Zeitsch. Nahr. Genussm. 1907, 14, 317) precipitates the neutralised, alcohol-free soap solution with barium chloride, and determines the baryta values for the soluble barium salts, and for the insoluble barium salts. He finds that normal butter has insoluble baryta value of 247 to 251, and soluble baryta value of 50 to 65. The value [insol. −(200+soluble)] is negative for butter, whereas other fats have a positive value not less than 39. (*See* also Fritzsche, Zeitsch. Nahr. Genussm. 1907, 14, 329.)

Ewers (*ibid.* 1910, 19, 529) proposes a method depending upon the different solubility of the magnesium salts of the fatty acids, and on the varying solubility in petroleum spirit of the fatty acids from the soluble magnesium salts.

Various methods have been proposed to distinguish between cocoa-nut fat and butter fat by means of the solubilities of the silver salts of the distilled acids in the Reichert-Wollny process (K. Jenson, Analyst, 1905, 30, 396; O. Jenson, Zeitsch. Nahr. Genussm. 1905, 10, 265; Kirschner, *ibid.* 1905, 9, 65; Wijsman and Reijst, *ibid.* 1906, 11, 267; Dean, Ann. Chim. anal. 1906, 11, 121).

Dons (Zeitsch. Nahr. Genussm. 1908, 15, 75) has modified the process. The mixed fatty acids are treated with water to remove the soluble portion. Caprylic acid, which remains behind with the insoluble acids, is removed by distillation, and estimated in the distillate by precipitation with silver nitrate solution. Pure butter-fat gives a value 1·6 to 2·0 and cocoa-nut fat 5·3.

Juckenack and Pasternack (Zeitsch. Nahr. Genussm. 1904, 7, 193) proposed to determine the presence of cocoa-nut oil in butter from the relationship between the Reichert - Wollny number and the saponification value. They point out that according to the formula [R.W. −(sapon. value−200)] butter fluctuates between −3·5 and +4·25. For cocoa-nut oil its value is −47. Harris (Analyst, 1906, 31, 355) has shown that the method of reasoning suggested is of no value for small admixtures of cocoa-nut fat with butter.

Paal and Amberger (Zeitsch. Nahr. Genussm. 1909, 17, 23) distil separated solid fatty acids in a current of steam in special flask, and precipitate the cadmium salts in distillate.

Hanuš (*ibid.* 1907, 13, 18) and Hanuš and Štekl (*ibid.* 1908, 15, 577) and Fendler (*ibid.* 1910, 19, 544) propose methods based upon the distillation of the ethyl esters of the fatty acids. Fendler prepares the esters after the manner of Henriques (Analyst, 1898, 23, 181) and collects the esters boiling below 300°. This fraction would include the ethyl esters of the acids up to and including myristic acid. The volume in the case of butter ranges from 2·5 to 6·1; cocoa-nut fat, 40 to 42; and lard, 0·5 to 1·1 c.c.

Caldwell and Hurtley (*l.c.*) state that small quantities of cocoa-nut fat can be detected by the fractional distillation in a high vacuum of the fatty acids.

(*b*) The foregoing tests for the detection of the adulteration of butter-fat are based upon the disturbance of the ratio existing in normal or average butter-fat between the proportions of soluble and insoluble acids. It has, however, been shown that special feeding may affect this relationship and produce butter giving abnormal results. Uncertainty as to the conclusions to be drawn may be removed if direct evidence is obtained from the application of specific tests. The following qualitative tests may be applied :—

Phytosterol test for detection of vegetable fats (Bömer, Zeitsch. Nahr. Genussm. 1901, 4, 1070, and 1902, 5, 1018).—The absolute alcohol extract of the unsaponifiable matter from 100 grams of fat is treated with acetic anhydride, the excess of which is removed, and the acetates dissolved in alcohol, crystallised, and recrystallised several times. Cholesteryl acetate melts at 113·5° to 114·5°, while the melting-point of Phytosteryl acetate is about 129°. If the melting-point of the mixed acetates from the sample under examination is between 116° and 117°, it is probably adulterated with vegetable fat; if above 117°, vegetable fat is certainly present. The test is not of value if paraffin wax is also present.

Hinks' test for cocoa-nut fat (Analyst, 1907, 32, 160).—5 c.c. of the fat are dissolved in 10 c.c. of ether, and the solution cooled in ice. After half an hour, it is rapidly filtered, the ether evaporated from the filtrate, and the fatty residue dissolved in 96 p.c. (vol.) alcohol. The solution is cooled to 5° for 15 minutes, filtered rapidly, and the filtrate cooled to 0°. The deposit which separates at this temperature is then examined on a cold slide under a power of about 250. Butter fat yields a deposit of round granular masses; cocoa-nut fat, fine needle-shaped crystals; and mixtures of butter and cocoa-nut fat, fine feathery crystals attached to the granular butter masses. The test is capable of detecting 5 p.c. of cocoa-nut fat in butter fat.

Badouin test for sesamé oil.—5 c.c. of the fat are mixed in a tube with 5 c.c. of HCl (sp.gr. 1·19) and 0·1 c.c. of a 2 p.c. furfural solution. The mixture is well shaken and allowed to stand. The aqueous layer which separates assumes a reddish colour in presence of sesamé oil. Butters coloured with some aniline dyes give with hydrochloric acid a pink-to-violet colouration, and in such a case the acid and fat mixture must be heated until colourless before the addition of the furfural solution.

Halphen test for cotton seed oil.—5 c.c. of the fat are dissolved in 5 c.c. of amyl alcohol, 1 c.c. of a solution of sulphur in carbon disulphide is added, and the mixture heated for 20 minutes at 105° in a brine-bath. A red colouration is produced in presence of cotton-seed oil. The chromogenetic substance may, however, in exceptional cases, be communicated to butter by feeding cows with cotton cake; and a positive reaction must be confirmed by other data of the examination.

(*c*) The specific gravity and the Zeiss reading should be taken and considered in conjunction with and relation to the data for the Reichert-

Wollny number, saponification and iodine values.

Of other physical methods there may be mentioned:

Valenta test.—3 c.c. of fat are dissolved in an equal volume of glacial acetic acid, and then allowed to cool while being stirred with a thermometer. Immediately a turbidity is noted, the temperature is read. A modification introduced by Jean is to measure the volume of acid dissolved in the fat at 50°.

Crismer test.—This method is an official one in Belgium. 0·5 c.c. of melted fat and 1 c.c. of absolute alcohol are placed in a tube fitted with cork and thermometer, the bulb of which dips into the liquid. The tube is gently heated inside a larger tube until the liquid becomes homogeneous. It is then allowed to cool, and the temperature noted when turbidity appears. This point is the critical temperature of dissolution (Crismer, Analyst, 1897, 22, 71).

3. **Examination for preservatives.**—(*a*) *Boron compounds.* Boric acid or borax is detected by moistening a strip of turmeric paper (filter paper soaked in an alcoholic solution of curcuma and dried) with a drop of water squeezed from the butter, or with the aqueous layer obtained on melting the butter. The paper is then dried. Free boric acid gives a pink colour changed to green with alkali. For borax a drop of dilute hydrochloric acid must be added to the paper before drying.

The boric acid is estimated by Richmond and Harrison's method (Analyst, 1902, 27, 179) or by washing the butter in a separator with hot water, evaporating the aqueous portion after addition of soda, incinerating, and proceeding as in Thomson's process.

A method suitable for rapid determinations is as follows: 10 grams of butter are shaken in a separator with 20 c.c. of hot water and 10 c.c. of decinormal sulphuric acid. The aqueous layer is run off after a few minutes, and the fat washed twice more with small quantities of hot water. The mineral acid in the combined water extracts is then neutralised, with lacmoid as indicator. 2 grams of mannite are now added, and phenolphthaleïn. Decinormal soda is then added until pink colour is permanent. The quantity of soda used after the solution was neutral to lacmoid indicates the proportion of boric acid present. A control experiment should be carried out with pure butter and indicators.

The Committee on Preservatives in Food recommended that borax or boric acid should be the only preservative allowed in butter, and that the quantity should not exceed 0·5 p.c. calculated as boric acid.

(*b*) *Formalin* is detected by the application of Hehner's test (Richmond, Analyst, 1896, 21, 92). A little milk is added to the aqueous layer from melted butter, and the mixture poured on to the surface of sulphuric acid containing a trace of ferric chloride. In presence of formaldehyde a blue ring appears at the juncture of the aqueous and acid layers.

(*c*) *Fluorides.* Fluorine is detected by evaporating the aqueous portion rendered alkaline from about 30 grams of butter, incinerating, and heating the ash in a platinum crucible with strong sulphuric acid. The crucible is covered with a watch-glass coated with wax through which a mark or design has been scratched with a fine instrument. In presence of fluoride the glass will be etched.

O. and C. W. Hehner (Analyst, 1902, 27, 173) indicate how to remove the boric acid if present before testing for fluoride.

(*d*) *Benzoic acid and benzoates.* 10 grams of butter are heated for some time with alcohol acidified with dilute sulphuric acid. The alcoholic extract, after dilution with water, is extracted with ether in a separator. The ether solution is then shaken with dilute ammonia, and the ammoniacal extract evaporated to dryness in a porcelain dish. The residue is dissolved in water, just acidified with acetic acid to ensure that no free ammonia remains, and a drop of ferric chloride solution added. Benzoic acid gives a buff-coloured precipitate.

(*e*) *Salicylic acid.* A portion of the alcoholic solution prepared for benzoic acid is tested directly with a drop of ferric chloride solution. Salicylic acid gives a violet colour.

(*f*) Richmond (Analyst, 1908, 33, 116) points out that formic acid and glucose are also used as preservative agents.

Colouring matters. The colour of butter prepared without addition of artificial colouring matter, varies according to the food of the cows. Winter butter from stall-fed cows is nearly colourless. Colouring matter is frequently added to butter during manufacture. Annatto, turmeric, carrot juice, saffron, marigold, safflower and aniline dyes are among the artificial colours employed. Agitation of the butter fat with hot alcohol will give an indication whether colour has been added. Cornelison (J. Amer. Chem. Soc. 1908, 30, 1478) shakes thoroughly 10 grams of melted fat with 10 to 20 grams of glacial acetic acid at about 35°. The acid layer is drawn off and tested with various reagents for the detection of aniline and vegetable dyes. Leeds (Analyst, 1887, 150) has also proposed a scheme for identification of dye.

Annatto and azo- dyes may be rapidly tested for as follows: 5 c.c. of melted fat are placed in each of two test-tubes. To one 5 c.c. of hydrochloric acid are added, and the mixture shaken. Azo- dyes will impart a reddish colour to the acid layer. To the second tube add 5 c.c. of ether, and shake, and then 5 c.c. of 10 p.c. potash solution. Shake and allow to separate. If annatto is present, the alkaline layer will be coloured yellow. To confirm the annatto, the alkaline liquid is withdrawn, evaporated to dryness, and touched with a drop of sulphuric acid. Annatto gives an indigo-blue to violet colouration.

Crampton and Simons (J. Amer. Chem. Soc. 1905, 27, 270) point out the use of palm oil as a colouring substance, and its detection by the Halphen and Liebermann-Storch methods for rosin oil.

The further examination of the butter is concerned with its flavour, appearance, rancidity. As regards rancidity, the quantity of free acid dissolved in alcohol may be ascertained, but this is frequently no guide to or measure of the rancidity, which is best judged by smell and taste.

The definition of 'butter' in the Margarine Act, 1887 (50 & 51 Vict. c. 29) is as follows: 'The word "butter" shall mean the substance usually known as butter, made exclusively from

milk or cream, or both, with or without salt or other preservative, and with or without the addition of colouring matter.'

The Butter and Margarine Act, 1907 (7 Edw. 7, c. 21) describes milk-blended butter as 'any mixture produced by mixing or blending butter with milk or cream (other than condensed milk or cream).' By the provisions of this Act milk-blended butter may contain a maximum of 24 p.c. of water.

'Renovated' or 'process' butter is a product mainly of the United States. It is defined by Act of Congress as 'butter which has been subjected to any process by which it is melted, clarified, or refined and made to resemble genuine butter.' Butter which is unsaleable through rancidity, mould growths, or other causes, is melted, and the oil separated from the curd and water. The oil is then aërated by 'blowing' with air, and afterwards emulsified with fresh milk inoculated with a bacterial culture. It is then churned and worked as for ordinary butter.

Crampton (J. Amer. Chem. Soc. 1903, 25, 358) gives details of analyses and tests. Several similar processes have been patented here, and in some factories the melting and purification of inferior butter is now carried on. Hence such products might contain crystalline fat, and the microscopical examination is now of no value as a test for foreign fat.

'Factory' butter is butter which has been reworked or blended with other butter; by 'dairy' butter is understood butter made at the farmer's homestead, whether from whole milk or cream; and the term 'creamery' butter is generally applied to butter made from cream separated by centrifugal force from the mixed milk of a number of herds in premises specially utilised for the purpose (*see* the Report of the Committee of the Department of Agriculture for Ireland, on the Irish Butter Industry, Cd. 5092, 1910).

In hot countries, owing to the rapid decomposition of ordinary butter, the clarified fat, free from water and curd, is prepared for sale, as schmelzbutter, ghee. G. S.

BUTTERINE *v.* MARGARINE.

BUTTER SUBSTITUTES *v.* MARGARINE.

BUTTER SURROGATE *v.* MARGARINE.

BUTTER, VEGETABLE. A greasy substance expressed from the kernel of the *Bassia butyracea* (Roxb.), a native of North India. This grease is said to make excellent soap. Shea butter is obtained from the *Butyrospermum Parkii*, of West Africa, and has been used in making candles and soap. The butter-tree of Sierra Leone is the *Pentadesma butyracea* (Subine), the fruit of which yields much grease, and is eaten by the negroes (*v.* OILS and FATS).

BUTTER YELLOW. *Benzeneazodimethyl aniline* $C_6H_5{\cdot}N:N{\cdot}C_6H_4{\cdot}N(CH_3)_2$. A yellow colouring matter (m.p. 115°); insoluble in water, soluble in dilute HCl, with red colour; soluble in fats. Used for colouring butter (Witt. Griess. Ber. 1877, 10, 528) (*v.* AZO- COLOURING MATTERS).

BUTTERS, MINERAL. A term formerly applied to several of the metallic chlorides, *e.g.* chlorides of antimony, tin, bismuth, zinc, &c.

BUTYL or TETRYL. A univalent radical yielding four isomeric mono- derivatives:

(1) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X$ (normal);
(2) $CH_3{\cdot}CH_2{\cdot}CHX{\cdot}CH_3$ (secondary);
(3) $(CH_3)_2CH{\cdot}CH_2X$;
(4) $(CH_3)_3CX$ (tertiary).

BUTYL COMPOUNDS.

Butyl alcohol. Tetryl alcohol C_4H_9OH. All the four possible bodies corresponding to this formula are known.

1. *Normal butyl alcohol: butanol; propyl carbinol* $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$; b.p. 115°, Lieben and Rossi (Compt. rend. 68, 1562) 117·2° (Brühl, Annalen, 203, 16); sp.gr. 0° = 0·8233, 20° = 0·8109, 40° = 0·7994, 98·7° = 0·7738, 20°/4° = 0·8099 (B.); $\mu_\alpha = 1{\cdot}39909$, mol. refraction = 35·45 (B.). Occurs in the heavy oil of Cognac brandy to the extent of 49 p.c. Is not formed in the fermentation of sugar produced by elliptical yeast (Claudon and Morin, Chem. Soc. Trans. 1887, ii. 714). Is produced by the action of sodium amalgam upon butyryl chloride and butyric acid (Saytzeff, Zeitsch. Chem. 1870, 108; Linnemann, Annalen, 161, 178). Also by the fermentation of glycerol by *Bacillus butylicus* and certain other bacteria in presence of calcium carbonate and various foodstuffs, *e.g.* ammonium tartrate; the yield amounts to 9 p.c. of the glycerol used. Butyric acid and a little ethyl alcohol are also formed (Fitz, Ber. 9, 1348; Vigna, Ber. 16, 1348). Is also produced by the action of nascent hydrogen (iron and acetic acid) upon crotonaldehyde and trichlorobutyraldehyde (Lieben and Zeisel, Monatsh. 1, 825, 842).

Beyerinck has shown that the *Bacillus butylicus* of Fitz (Ber. 1882, 867) is in reality the butyric ferment. The true butylic ferment, *Granulobacter butylicum*, has been isolated in a pure condition, and an account of the whole fermentation process is given (J. Soc. Chem. Ind. 1894, 167; *ibid.* 969). (*See* also Emmerling, Ber. 1896, 2726; 1897, 451; Buchner and Meisenheimer, Ber. 1908, 1410.)

Properties.—Colourless liquid, soluble in 12 parts of water, from which solution it can be separated by means of calcium chloride. Soluble in concentrated hydrochloric acid; is readily oxidised to butyric acid. Fused zinc chloride abstracts water, and yields β-butylene and smaller amounts of normal butylene (Le Bel and Greene, Amer. Chem. J. 2, 24).

Bromine acting on *n*-butyl alcohol yields, with some difficulty, mono-brombutaldehyde, b.p. 235° (Étard, Compt. rend. 114, 753). The action of aluminium amalgam on the butyl alcohols, producing liquid aluminium alkoxides, has been studied by Tistshenko (Chem. Soc. Abstr. 1899, i. 408).

2. *Iso-butyl alcohol, isopropyl carbinol-α-hydroxy β-methylpropane* $(CH_3)_2CH{\cdot}CH_2OH$, b.p. 108·4° (Linnemann, Annalen, 160, 238); sp.gr. 0·7265 at 106·6°/4° (Schiff, Annalen, 220, 102), 0·8168 at 0° (L.), 0·8069 at 15°/15°, 0·8008 at 25°/25° Perkin (Chem. Soc. Trans. 1884, 468); sp. heat = 0·686; molecular rotation = 4·936 at 17·7° (P.); molecular refraction = 35·41; $\mu_\beta = 1{\cdot}4007$. Sp.gr. of aqueous solutions (Duclaux, Ann. Chim. Phys. [5] 13, 91):

Percentage of alcohol (by vol.)	2·5	5	6	10
Sp.gr. of aqueous solution at 15°	0·9950	0·9930	0·9915	0·9875

Occurs in fusel oil from potatoes and beet (Wurtz, Ann. Chim. Phys. [3] 42, 129), and combined with angelic and *iso*butyric acids in Roman oil of chamomile (Köbig, Annalen, 195, 96).

Preparation.—By the action of sodium amalgam and water upon β-chlor*iso*butyl alcohol, which results from the action of hypochlorous acid upon *iso*butylene (Butlerow, Annalen, 144, 24). Is formed in small quantity by the action of elliptical yeast upon sugar or glycerol (Claudon and Morin, Chem. Soc. Trans. 1887, ii. 714). By the reduction of *iso*butyric aldehyde with sodium amalgam (Linnemann and Zotta, Annalen, 162, 11).

Properties.—Colourless liquid, soluble in 10·5 parts of water, from which calcium chloride causes it to separate. Smells like fusel oil. Is oxidised by chromic acid into *iso*butyric acid, acetic acid, carbon dioxide, acetone, and other products (Krämer, Ber. 7, 252; Schmitt, *ibid.* 8, 1361). Zinc-dust yields water and *iso*butylene (Jahn, *ibid.* 13, 989).

Treated with iodine and aluminium, aluminium tri*iso*butoxide $Al(C_4H_9O)_3$ is formed. It is a liquid which may be distilled *in vacuo* (Gladstone and Tribe, Chem. Soc. Trans. 1881, 6).

*Iso*butyl alcohol may be catalytically oxidised to *iso*butyl aldehyde. The vapour of the alcohol mixed with air, is passed over warm freshly reduced copper spirals and the products collected. A yield of 50 p.c. is obtainable (E. Orlow, J. Soc. Chem. Ind. 1908, 957).

When chlorine is passed into dry *iso*butyl alcohol, and the solution subsequently heated gently, the product can be separated into two fractions, boiling at 80°–100° and 170°–250°. The lower fraction consists of *chlorisobutaldehyde*, boiling at 90°–91°; sp.gr. 1·186, 15°/4°. It combines with sodium hydrogen sulphite, and when oxidised with alkaline permanganate yields acetone and hydroxy*iso*butyric acid $C(CH_3)_2OH\cdot COOH$, melting at 78°. A termolecular polymeride $C_{12}H_{21}Cl_3O_3$, which melts at 107°, is obtained by shaking with strong sulphuric acid (A. Brochet, Compt. rend. 114, 1538). If the alcohol is kept cold, the chief product is *dichlorisobutyl oxide* $C(CH_3)_2Cl\cdot CHCl\cdot O\cdot CH_2CH(CH_3)_2$ boiling at 192·5°/760, and of sp.gr. 1·031, 15°/4°. Water is without action on this product at low temperatures, but at 100° produces hydrogen chloride and α-chlor*iso*butaldehyde and di*iso*butylmonochlor*iso*butyral $C(CH_3)_2Cl\cdot CH(OC_4H_9)$ boiling at 218°, and of sp.gr. 0·9355, 15°/4° (A. Brochet, Compt. rend. 118, 1280; *v.* also Brochet, Bull. Soc. chim. 1896, 16; *ibid.* 20).

When chlorine is led into hot *iso*butyl alcohol, chlor*iso*butyric*iso*butyl ester, αβ-dichlor*iso*butyric acid, *iso*butyl ester, mono- and dichlor-*iso*butyric aldehyde, *iso*butyric acid, oxy*iso*butyric acid, crotonic acid CO,CO_2, and methyl chloride are produced. Treating aqueous *iso*butyl alcohol with chlorine water produces *iso*butyric acid, and α-chlor*iso*butyric acid *iso*butyl ester. Chlorine acting on cold dry *iso*butyl alcohol in the light produces 1 : 2-dichlor*iso*butyl ester (Brochet, Ann. Chim. Phys. [7] 10, 363).

*Iso*butyl alcohol, when acted on by bromine, readily yields *iso*butyl bromide, mixed with *iso*butyl *iso*butyrate, and brom*iso*butaldehyde (Étard, Compt. rend. 114, 753).

(For combinations and derivatives of *iso*butyl alcohol, *v.* Gladstone and Tribe, Chem. Soc. Trans. 1881, 6; Pierre and Puchot, Annalen, 163, 274; and Heindl, Monatsh. 2, 208.)

3. *Secondary butyl alcohol, 2-hydroxybutane, methyl ethyl carbinol, butylene hydrate.* $\begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>\!\!CHOH$; b.p. 99° at 738·8 mm. (Lieben, Annalen, 150, 114); sp.gr. 0·827 at 0°, 0·810 at 22° (L.).

Formed by the action of water upon the compound of zinc-ethyl and aldehyde:

$$CH_3CH(C_2H_5)O\cdot Zn(C_2H_5)$$

thus:

$$CH_3CH(C_2H_5)O\cdot ZnC_2H_5+H_2O = C_4H_9OH+ZnO+C_2H_6$$

(Wagner, Annalen, 181, 261). Also by acting upon secondary butyl iodide with silver acetate and saponifying the resulting acetate by means of potash. Normal butyl alcohol may be changed into the secondary alcohol; the normal iodide is heated with potash, and the normal butylene so obtained on treatment with hydriodic acid yields secondary butyl iodide (Saytzeff, Zeitsch. anal. Chem. 1870, 327). It may also be prepared from the normal isomeride by treating *n*-butylamine with nitrous acid (Meyer, Ber. 10, 130; Kanonnikoff and Saytzeff, Chem. Soc. Trans. 1875, 626).

Properties.—Liquid, with strong odour; upon oxidation yields a ketone $C_2H_5\cdot CO\cdot CH_3$ (b.p. 80°), and acetic acid (Kanonnikoff and Saytzeff, Chem. Soc. Trans. 1875, 626). Heated with a trace of hydrochloric, hydrobromic, or hydriodic acid, in a sealed tube, to 240°, yields C_4H_8 (pseudo-butylene). It has been separated into its optical antipodes by R. Meth (Ber. 1907, 695); the alcohol has $[\alpha]_D$, 0·32°.

4. *Tertiary butyl alcohol, trimethyl carbinol* $(CH_3)_3C\cdot OH$. A solid; m.p. 25·45° (De Forcrand, Compt. rend. 136, 1034); b.p. 82·94° (corr.) (Linnemann, Annalen, 162, 26); 81·5°–82° (Perkin, Chem. Soc. Trans. 1884, 468). Sp.gr. 0·7792 at 37° (L.); 0·7788 at 30° (Butlerow, Annalen, 162, 229); 0·7864 at 20°/4°, 0·7802 at 26°/4° (Brühl, Annalen, 203, 17); 0·7836 at 25°/25°, 0·7761 at 35°/35°; molecular rotation at 24·3° = 5·122 (P.); $\mu_\beta = 1{\cdot}3924$; molecular refraction = 35·53; crit. temp. = 234·9° (Pawlewski, Ber. 16, 2634).

Formed from *iso*butyl iodide by treatment with acetic acid and silver oxide (Linnemann; Butlerow, Annalen, 168, 143); also from *iso*butylamine by treatment with nitrous acid, and from *iso*butyl carbimide $CO\cdot N\cdot C_4H_4$, by action of potash (Linnemann, Annalen, 162, 12). Can be prepared by allowing 20 grams of tertiary butyl iodide and 50 grams of water to stand in contact for two or three days (Dobbin, Chem. Soc. Trans. 1880, 238).

*Iso*butyl alcohol heated with excess of hydrochloric acid yields a mixture of secondary and tertiary butyl chlorides, and when heated with six volumes of water only the latter is decomposed, yielding the alcohol and hydrochloric acid (Freund, J. Pharm. Chim. [2] 12, 25).

Properties.—Forms rhombic plates or prisms. Unites with water to form a liquid hydrate $2C_4H_{10}O,H_2O$ (b.p. 80°; sp.gr. 0·8276 at 0° (Butlerow, Annalen, 162, 229). On oxidation

yields acetone, carbon dioxide, acetic acid, and a small quantity of *iso*butyric acid (Butlerow, Zeitsch. Chem. 1871, 485).

The existence of the hydrate $C_4H_{10}O,2H_2O$, m.p. 0°, is confirmed by cryoscopic, density and viscosity determinations (Paternò and Mieli, *Atti. R. Accad. Lincei.* 1907 (v.), 16, ii. 153).

In sunlight it combines with chlorine, forming tertiary butyl chloride and other substances (D'Otreppe, J. 1881, 512).

Trimethyl carbinol explodes feebly when treated with bromine, yielding *isobutylene bromide* $C(CH_3)_2Br{\cdot}CH_2Br$ boiling at 148° (Étard, Compt. rend. 114, 753).

Tertiary butyl alcohol has a slightly narcotic action when taken internally, and is found in the urine in combination with glycuronic acid (Thierfelder and v. Mering, Chem. Soc. Abstr. 1885, i. 1002).

Nitrohydroxybutanes may be obtained quantitatively as follows: By the action of nitromethane on formaldehyde, in presence of a little potassium carbonate, tertiary nitrotrihydroxybutane $NO_2{\cdot}(CH_2OH)_3$, a white crystalline solid, melting at 158°–159°, is produced. Nitroethane produces tertiary nitrodihydroxybutane $NO_2{\cdot}C(CH_3)(CH_2OH)_2$, melting at 139°–140°. Secondary nitropropane yields nitro*iso*butyl alcohol $NO_2{\cdot}C(Me)_2{\cdot}CH_2OH$, melting at 82° (L. Henry, Compt. rend. 1895, 121, 210).

Butyl bromides. Tetryl bromides C_4H_9Br.

1. *Normal butyl bromide, α-bromobutane*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$;

b.p. 99·9° (corr.) (Linnemann, Annalen, 161, 193); sp.gr. 1·3050 at 0°, 1·2792 at 20°, 1·2571 at 40° (Lieben and Rossi, *ibid.* 158, 161).

Formed from normal butyl alcohol and hydrobromic acid (L. and R.).

By the action of bromine, *αβ*-dibrombutane $C_4H_8Br_2$ (b.p. 166°) is formed (L.).

2. *Isobutyl bromide, α*-bromo-*β*-methyl propane $(CH_3)_2CH{\cdot}CH_2Br$; b.p. 92·3° (corr.) (Linnemann, Annalen, 162, 34); 91·3° (Perkin, Chem. Soc. Trans. 1884, 459); sp.gr. 1·2038 at 16° (L.), 1·2722 at 15°/15°, 1·2598 at 25°/25° (P.). Molecular rotation = 8·003 at 16·2° (P.). From *iso*butyl alcohol, bromine, and phosphorus (Wurtz, Annalen, 93, 114). Unites with bromine at 150° to form $C_4H_7Br_3$ (L.).

3. *Tertiary butyl bromide, β-bromo-β-methyl propane* $(CH_3)_3CBr$; b.p. 72° at 761·5 mm.; sp.gr. 1·215 at 20°, 1·2020 at 15°/15°, 1·1892 at 25°/25°; molecular rotation = 8·238 at 17·8° (P.). Formed when *iso*butyl bromide is heated to 240° (Eltekow, Ber. 8, 1244). Also from trimethyl carbinol and phosphorus pentabromide (Reboul, J. 1881, 409). May also be prepared by leading *iso*butylene into a solution of hydrobromic acid of sp.gr. 1·7 (Roozeboom, Ber. 14, 2396). Is readily decomposed at 300° into *iso*butylene and hydrobromic acid. Water, in the cold, forms the alcohol.

4. *Secondary butyl bromide, β-brombutane* $CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$; b.p. 90°–93° (V. Meyer and Müller, J. pr. Chem. [2] 46, 183); obtained from secondary butyl alcohol by the action of hydrobromic acid, and yields *β* (*γ*)-dibrombutane by warming with iron and bromine.

Butyl chlorides. Tetryl chlorides C_4H_9Cl.

1. *Normal butyl chloride, α-chlorbutane*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$;

b.p. 77·96° (corr.) (Linnemann, Annalen, 61, 197); sp.gr. 0·9074 at 0°, 0·8874 at 20° (Lieben and Rossi, *ibid.* 158, 161); 0·9074 at 0° (L.), 0·8972 at 14°. Formed by the action of chlorine upon *n*-butane (Pelouze and Cahours, J. 1863, 524). More easily by the action of hydrochloric acid upon *n*-butyl alcohol (Lieben and Rossi).

2. *Isobutyl chloride, β-methyl-α-chlorpropane* $(CH_3)_2CH{\cdot}CH_2Cl$; b.p. 68·5° (Linnemann, Annalen, 162, 17); 68·5°–69° (Perkin, Chem. Soc. Trans. 1884, 451); sp.gr. 0·8798 at 15° (L.), 0·8953 at 0°, 0·8651 at 27·8°, 0·8281 at 59° (Pierre, Puchot, Annalen, 163, 276), 0·8835 at 15°/15°, 0·8739 at 25°/25° (P.). Molecular rotation at 21·3° = 6·144 (Perkin). Formed by the action of hydrochloric acid or PCl_5 upon the alcohol (Wurtz, *ibid.* 93, 113). By the action of chlorine, hexachlorbutane is produced.

*Iso*butyl chloride is also produced by the interaction of chlorine and *iso*butane in diffused sunlight (Mabery and Hudson, Amer. Chem. J. 19, 245); and also by treating *iso*butylamine cooled to −15° with nitrosyl chloride (Solonina, Chem. Zentr. 1898, ii. 887).

3. *Tertiary butyl chloride, β-methyl-β-chlorpropane* $(CH_3)_3CCl$; b.p. 51°–52° (Perkin, Chem. Soc. Trans. 1884, 451); sp.gr. 0·8658 at 0° (Puchot), 0·8471 at 15°/15°, 0·8368 at 25°/25°; molecular rotation at 15° = 6·257 (Perkin).

Formed (1) by the chlorination of tertiary butane (Butlerow); (2) by the action of iodine monochloride upon *iso*butyl iodide (Linnemann, Annalen, 162, 18); (3) by the action of hydrochloric acid upon *iso*butylene at 100° (Zalessky, Ber. 5, 480; Le Bel, Bull. Soc. chim. 28, 462); (4) by saturating trimethyl carbinol at 0° with HCl gas (Schramm, Monatsh. 9, 619).

Heated with five or six vols. of water to 100°, the alcohol is produced (Butlerow, Annalen, 144, 33). Chlorine in diffused daylight, in the cold, forms $C_4H_8Cl_2$ (b.p. 106°–107°), $C_4H_7Cl_3$ and $C_4H_5Cl_5$, whilst in direct sunlight $C_4H_4Cl_6$ (b.p. in partial vacuum about 115°), and other products are formed (D'Ottreppe, J. 1882, 441).

Tertiary butyl chloride is also formed by the action of PCl_5 on trimethyl carbinol (Janschenko, Chem. Zentr. 1897, ii. 334). It also results, together with *iso*butyl chloride from the action of nitrosyl chloride on tertiary butylamine in xylene solution at −15° to −20° (Salonina, *ibid.* 1898, ii. 888).

4. *Secondary butyl chloride, β-chlorobutane* $CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3$, is produced by the action of nitrosyl chloride on secondary butylamine in xylene solution at −20° (Solonina, Chem. Zentr. 1898, ii. 888).

Butyl cyanates. Only the *iso*-cyanates have been described.

1. *Isobutyl isocyanate. Iso*butyl carbimide $(CH_3)_2CH{\cdot}CH_2{\cdot}NCO$; b.p. 110° obtained by the distillation of *iso*butyl iodide with silver cyanate and sand (Brauner, Ber. 12, 1877).

2. *Tertiary butyl isocyanate*

$(CH_3)_3C{\cdot}NCO$;

b.p. 85·5° (corr.); sp.gr. 0·8676 at 0°; remains liquid at −25°. Is formed, together with other substances, when silver cyanate acts upon *iso*butyl iodide (Brauner, Ber. 12, 1874). By the action

of hydrochloric acid, forms tertiary butylamine $(CH_3)_3C{\cdot}NH_2$. Potash produces symmetrical di*iso*butyl urea, melting at 242°.

Butyl cyanides. C_4H_9CN.

1. *Normal butyl cyanide, valeronitrile*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2CN$;

b.p. 140·4° at 739·3 mm.; sp.gr. 0·8164 at 0° (Lieben and Rossi, Annalen, 158, 171).

2. *Isobutyl cyanide* $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CN$; b.p. 126°–128° at 714 mm. (Erlenmeyer and Hell, Annalen, 160, 266); 129·3°–129·5° at 764·3 mm. (R.Schiff, Ber. 19,567); sp.gr. 0·8227 at 0°, 0·8069 at 20° (Erlenmeyer and Hell); 0·6921 at 129°/4° (S.). Formed by the oxidation of gelatin (Schlieper, Annalen, 59, 15) or casein (Gunckelberger, *ibid.* 64, 76) with chromic acid; also by the action of P_2O_5 upon ammonium *iso*valerate (Dumas, Malaguti, and Leblanc, *ibid.* 64, 334). May be prepared by heating 300 grams *iso*butyl iodide, 98 grams of potassium cyanide, 98 grams of alcohol, and 25 grams of water for three days on the water-bath (Erlenmeyer and Hell).

3. *Tertiary butyl cyanide* $(CH_3)_3C{\cdot}CN$; m.p. 15°–16°; b.p. 105°–106°. Formed by mixing 100 parts of tertiary butyl iodide, 110 parts of mercury potassium cyanide $Hg(CN)_2{\cdot}2KCN$ with 75 parts of dry magnesia, and allowing the mixture to remain for two or three days at a temperature not exceeding 5°. The mass is then treated with water, and distilled on the paraffin-bath (Butlerow, Annalen, 170, 154).

4. *Secondary butyl cyanide*, methylethyl acetonitrile $C_2H_5{\cdot}CH_3{\cdot}CH{\cdot}CN$; b.p. 125°; sp.gr. 0·8061 at 0°. Sodium (½ eqv.) is dissolved in acetonitrile in benzene, and ethyl iodide (1 eqv.) added (Hanriot and Bouveault, Bull. Soc. chim. (3), 1, 172).

Butyl hydrides. Butanes, tetranes.

1. *Normal butane, diethyl, methylpropane* $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$; b.p. 1° (Butlerow, Zeitsch. Chem. 1867, 363); sp.gr. 0·60 at 0° (Ronalds, Chem. Soc. Trans. 1865, 54). Occurs in crude petroleum (Ronalds, Lefebvre, Zeitsch. Chem. 1869, 185). Formed by heating ethyl iodide with zinc to 150° (Frankland, Annalen, 71, 173; Schöyen, *ibid.* 130, 233). Also by the action of sodium amalgam upon ethyl iodide (Löwig, J. 1860, 397). A colourless gas, insoluble in water. 1 vol. of alcohol at 14·2° and 744·8 mm. absorbs 18·13 vols. of butane (Frankland).

2. *Isobutane, trimethylmethane* $(CH_3)_3CH$; b.p. −17°. Formed by heating 0·9 part of *iso*butyl iodide with 2·4 parts of aluminium chloride to 120° (Köhnlein, Ber. 16, 562). Also by the action of zinc and water upon tertiary butyl iodide (Butlerow, Annalen, 144, 10). The gas is readily soluble in alcohol, from which it can be expelled by dilution with water.

3. *Cyclobutane*, tetramethylene, $\begin{matrix} CH_2-CH_2 \\ | \quad | \\ CH_2-CH_2 \end{matrix}$ has not yet been obtained, but many derivatives have been prepared by Perkin (Chem. Soc. Trans. 1893, 693; 1894, 950).

Butyl iodides. Tetryl iodides C_4H_9I.

1. *Normal butyl iodide*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2I$;

b.p. 129·8° (corr.) (Linnemann, Annalen, 161, 196); 130·4°–131·4° at 745·4 mm. (Brühl, *ibid.* 203, 21); sp.gr. 1·643 at 0°, 1·6136 at 20° (Lieben and Rossi, *ibid.* 158, 163), 1·6166 at 20°/4° (Brühl). From *n*-butyl alcohol and hydriodic acid (Linnemann, *ibid.* 161, 196). By the action of iodine trichloride at 250° it yields hexachlorethane C_2Cl_6 (Krafft, Ber. 10, 805).

2. *Isobutyl iodide, α-iodo-β-methylpropane* $(CH_3)_2{\cdot}CH{\cdot}CH_2I$; b.p. 120·0° (corr.) (Linnemann, Annalen, 160, 240; 192, 69); 83°–83·25° at 250 mm. (Perkin, Chem. Soc. Trans. 1884, 451); sp.gr. 1·6401 at 0° (L.), 1·6056 at 20°/4° (Brühl, Annalen, 203, 21), 1·6138 at 15°/15°, 1·6007 at 25°/25° (P.). Molecular rotation at 19·4°=12·199 (P.). From *iso*butyl alcohol, phosphorus, and iodine (Wurtz, Annalen, 93, 116).

3. *Secondary butyl iodide, β-iodobutane*

$C_2H_5{\cdot}CHI{\cdot}CH_3$;

b.p. 117°–118° (Luynes, Bull. Soc. chim. 2, 3); 119°–120° (Lieben, Annalen, 150, 96); sp.gr. 1·6263 at 0°/0°, 1·5952 at 20°/0°, 1·5787 at 30°/0° (Lieben). Formed by distilling erythritol with hydriodic acid (Luynes) or from *n*-butylene and hydriodic acid (Wurtz, Annalen, 152, 23). (See also Clarke, Chem. Zentr. 1908, ii. 1015.)

4. *Tertiary butyl iodide, β-methyl-β-iodopropane* $(CH_3)_3CI$; b.p. 98°–99° (with decom.) (Butlerow); 100·3° (Puchot, Ann. Chim. Phys. [5] 28, 546); sp.gr. 1·571 at 0°, 1·479 at 53° (P.). From tertiary butyl alcohol and hydriodic acid or *iso*butylene and hydriodic acid (Butlerow, Annalen, 144, 5, 22); is easily decomposed (by silver oxide, potash, or by heating with zinc and water), into hydriodic acid and *iso*butylene (Butlerow, Zeitsch. Chem. 1867, 362). Is also decomposed by water in the cold, yielding hydriodic acid and tertiary butyl alcohol. On heating with sodium, yields a mixture of hydrogen, *iso*butylene, and tri*iso*butylene ($C_{12}H_{24}$) (Dobbin, Chem. Soc. Trans. 1880, 236).

Butyl mercaptans $C_4H_9{\cdot}SH$.

1. *Normal butyl mercaptan*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SH$;

b.p. 97°–98°; sp.gr. 0·858 at 0° (Saytzeff and Grabowsky, Annalen, 171, 251; 175, 351).

2. *Isobutyl mercaptan*

$(CH_3)_2CH{\cdot}CH_2SH$;

b.p. 88°; sp.gr. 0·848 at 11·5° (Humann, Annalen, 95, 256), 0·83573 at 20°/4° (Nasini, Ber. 15, 2882).

3. *Secondary butyl mercaptan*

$C_2H_5{\cdot}CH(SH)CH_3$;

b.p. 84°–85°; sp.gr. 0·8299 at 17°. The mercury compound $(C_4H_9S)_2Hg$ melts at 189° (Reymann, Ber. 7, 1287).

4. *Tertiary butyl mercaptan*

$(CH_3)_3C{\cdot}SH$

is prepared from tertiary butyl iodide, zinc sulphide, and alcohol (Dobbin, Chem. Soc. Trans. 1890, 641). It boils at 65°–67°, and solidifies in a freezing mixture.

Butyl nitrates.

1. *Normal butyl nitrate*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$;

boils at 136°; sp.gr. 1·048 at 0° (Bertoni, Gazz. chim. ital. 20, 374).

2. *Isobutyl nitrate* $(CH_3)_2CH{\cdot}CH_2{\cdot}O{\cdot}NO_2$ b.p. 123°; sp.gr. 1·0384 at 0°, molecular rotation at 8·9°=5·18 (P.); molecular refraction=46·72 (P.); b.p. 123·5°–124·5° (Perkin, Chem. Soc. Trans.

1889, 684), sp.gr. 1·0334 at 4°/4°, 1·0264 10°/10°, 1·0124 25°/25° (P.). From silver nitrate, urea, and *iso*butyl iodide (Wurtz, Annalen, 93, 120; Chapman and Smith, Zeitsch. Chem. 1869, 433).

3. *Secondary butyl nitrate* boils at 124°; sp.gr. 1·0382 at 0° (Bertoni, Gazz. chim. ital. 20, 375).

Butyl nitrites, nitrobutanes $C_4H_9NO_2$.

1. *Isobutyl nitrite* $(CH_3)_2CH{\cdot}CH_2{\cdot}NO_2$; b.p. 67°; sp.gr. 0·89445 at 0° (Chapman and Smith, Zeitsch. Chem. 1869, 433), 0·8878 at 4°/4°, 0·8806 at 10°/10°, 0·8752 at 15°/15°, 0·8702 at 20°/20°, 0·8652 at 25°/25°; molecular rotation at 8·2°=5·51; molecular refraction =43·9 (Perkin, Chem. Soc. Trans. 1889, 686 and 757). Prepared by mixing *iso*butyl alcohol and sulphuric acid, and gradually pouring the cooled mixture, into an aqueous solution of sodium nitrite (1 : 3); the upper layer, consisting of *iso*butyl nitrite, is decanted, washed with potassium carbonate solution, and dried. It is a pale-yellow liquid, is apt to become acid by keeping, when rapid decomposition sets in. Taken medicinally, lowers the blood pressure and produces respiratory paralysis (Dunstan and Woolley, Pharm. J. [3] 19, 487).

2. *Tertiary butyl nitrite* $(CH_3)_3C{\cdot}NO_2$; b.p. 63°; sp.gr. 0·8914 at 0° (Bertoni, Gazz. chim. ital. 15, 351); 67°–68° (Tscherniak, Annalen, 180, 155). From the alcohol and glyceryl nitrite (B.); also from the iodide and silver nitrite (T.). A yellow, mobile liquid; soluble in alcohol, ether, and chloroform; sparingly soluble in water.

Aromatic nitrobutyl derivatives.

The butyl derivatives of many aromatic nitrohydrocarbons have a musk-like odour, and are sold as 'artificial musk.' *Musk Baur*, trinitro *meta*butyl toluene $C_6H(CH_3)(NO_2)_3C(CH_3)_3$, is formed by nitrating *meta* butyl toluene with fuming nitric and fuming sulphuric acids. Butyl toluene is formed by Friedel and Craft's method, as described below, by the action of tertiary butyl bromide on toluene in the presence of aluminium chloride. Butyl benzene, ethyl benzene, and xylene are formed at the same time.

An unsymmetrical butyl cresol is formed by adding butyl alcohol and zinc chloride to meta-cresol. When etherified and nitrated, possesses the odour of civet (A. Baur, J. Soc. Chem. Ind. 1892, 307; Dingl. poly. J. 273, 522; J. Soc. Chem. Ind. 1894, 1218).

Butyl xylene may be prepared by passing a current of *iso*butylene gas through a mixture of 5 kilos. *m*-xylene, 50 grams *iso*butyl chloride, and 200 grams aluminium chloride at 10°. The product is washed with water, and the fraction of the oil boiling at 200°–302° collected. Gaseous hydrochloric and hydrobromic acids may be employed to start the reaction (Act. Gesell. für Anilin-Fabriken, Fr. Pat. 372603).

Butyl ethers $(C_4H_9)_2O$.

1. *Normal butyl ether*; b.p. 140·5° at 741·5 mm. (Lieben and Rossi, Annalen, 165, 110); sp.gr. 0·784 at 0°, 0·7685 at 20° (L. and R.), 0·7865 at 0° (Douiner, Annalen, 243, 8). By the action of the sodium derivatives of the alcohol upon *n*-butyl bromide (Reboul, Compt. rend. 108, 39).

2. *Isobutyl ether* $[(CH_3)_2CH{\cdot}CH_2]_2O$; b.p. 122°–122·5° (Reboul, Compt. rend. 108, 162); sp.gr. 0·7616 at 15° (R.). From *iso*butyl bromide and sodium *iso*butylate (R.). The action of *iso*butyl iodide upon potassium *iso*butylate—which, according to Wurtz, yields this ether—really gives a mixture of di*iso*butylene and *iso*butyl alcohol (Reboul).

3. *Secondary butyl ether*

$[C_2H_5{\cdot}CH(CH_3)]_2O$;

b.p. 120°–121°; sp.gr. 0·756 at 21° (Kessel, Annalen, 175, 50). From ethylidene chlorhydrin, and zinc ethyl (K.). Formed in mere traces only by the action of secondary butyl bromide upon the sodium derivative of the secondary alcohol (Reboul, Compt. rend. 108, 162). Reboul obtained also the following mixed ethers:—

Secondary butyl *iso*butyl ether; b.p. 121°–122°; sp.gr. 0·7652 at 21°;

Normal butyl *iso*butyl ether; b.p. 131·5°; sp.gr. 0·763 at 15·5;

Normal butyl secondary butyl ether; b.p. 131°; sp.gr. 0·7687 at 15°;

Normal butyl tertiary butyl ether; b.p. 124°; but could not obtain the secondary, tertiary, and the ditertiary ethers (Bull. Soc. chim. [3] 2, 25).

Butyl sulphides.

1. *Normal butyl sulphide*

$[CH_3(CH_2)_3]_2S$;

b.p. 182°; sp.gr. 0·8523 at 0° (Saytzeff, Annalen, 171, 253). From butyl iodide and potassium sulphide. Fuming nitric acid yields the sulphone $(C_4H_9)_2SO_2$ (m.p. 43·5°) (Grabowsky, Annalen, 175, 348). Nitric acid of sp.gr. 1·3 converts it into the oxide $(C_4H_9)_2SO$, melting at 32°.

2. *Isobutyl sulphide* $[(CH_3)_2CH{\cdot}CH_2]_2S$; b.p. 172°–173° at 747 mm. (Grabowsky and Saytzeff, Annalen, 171, 254), 170·5° at 752 mm. (Beckmann, J. pr. Chem. [2] 17, 445); sp.gr. 0·8363 at 10° (B.).

Isobutyl disulphide $(C_4H_9)_2S_2$; b.p. 220° (Spring and Legros, Ber. 15, 1940).

3. *Secondary butyl sulphide*

$(CH_3{\cdot}CH{\cdot}C_2H_5)_2S$;

b.p. 165°; sp.gr. 0·8317 at 23° (Reymann, Ber. 7, 1288).

Butyl thiocarbimides. Butyl mustard oils; *iso*thiocyanates.

1. *Normal butyl thiocarbimide*

$(C_4H_9)NCS$;

b.p. 167° (Hofmann, Ber. 7, 512). From *n*-butylamine, carbon disulphide, and alcohol (H.).

2. *Isobutyl thiocarbimide*

$(CH_3)_2CH{\cdot}CH_2{\cdot}NCS$;

b.p. 162°; sp.gr. 0·9638 at 14° (Hofmann, Ber. 7, 511).

3. *Secondary butyl thiocarbimide*

$C_2H_5{\cdot}CH(CH_3)NCS$;

b.p. 159·5°; sp.gr. 0·944 at 12°. Occurs in the ethereal oil from spoonwort (*Cochlearia officinalis*) (Hofmann, Ber. 2, 102; 7, 512).

4. *Tertiary butyl thiocarbimide*

$(CH_3)_3C{\cdot}NCS$;

m.p. 10·5°; b.p. 140° at 770·3 mm.; sp.gr. 0·9187 at 10°, 0·9003 at 34° (Rudnew, Bull. Soc. chim. 1880, 300). Has a pleasant aromatic odour.

BUTYLAMINES.

1. Monobutylamines.

(*a*) *Normal butylamine, aminobutane*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$;

b.p. 75·5° at 740 mm. (Lieben and Rossi, Annalen, 158, 172); sp.gr. 0·7553 at 0°, 0·7333 at 26° (L. and R.), 0·7401 at 20° (Linnemann and Zotta, Annalen, 162, 3). Formed by the action of potassium hydroxide upon butyl cyanate (Lieben and Rossi); also from propyl cyanide by zinc and sulphuric acid (Linnemann and Zotta, Annalen, 162, 3), or from nitrobutane by action of tin and hydrochloric acid (Züblin, Ber. 10, 2083). Is miscible with water; reduces copper, silver, and mercury solutions in presence of alkalis. The chloride forms a yellow crystalline compound with $PtCl_4$, which is almost insoluble in cold water.

(*b*) *Isobutylamine, α-amino-β-methylpropane* $(CH_3)_2CH{\cdot}CH_2{\cdot}NH_2$; b.p. 68° (Schiff, Ber. 19, 565), 68°–69° (Perkin, Chem. Soc. Trans. 55, 694); sp.gr. 0·7357 at 55° (Linnemann, Annalen, 162, 23), 0·7464 at 4°/4°, 0·7408 at 10°/10°, 0·7363 at 15°/15°, 0·7283 at 25°/25°; mol. rot. at 15·3° 5·692; heat of combustion 726,990. From *iso*butyl cyanate and potash (Linnemann, Annalen, 162, 23); also from *iso*butyl iodide and ammonia (Hughes and Romer, Ber. 7, 511); also from *iso*butyl chloride and ammonia dissolved in water or *iso*butyl alcohol. All three *iso*butylamines are produced, the tri*iso*butylamine in largest quantity. The bases can then be separated by means of ethyl oxalate. The product is first separated into two fractions, the one rich in the mono*iso*butylamine, the other rich in the di- and tri- compounds. To the former water and then ethyl oxalate are added; the primary base is thus converted into the oxamide $C_2O_2(NHC_4H_9)_2$, which is almost insoluble in boiling water, the secondary amine being changed into the ethyl oxamate $C_2H_5O{\cdot}C_2O_2{\cdot}N(C_4H_9)_2$. The other fraction (anhydrous) being poured into ethyl oxalate, the primary and secondary bases are converted into oxamates. The tertiary base is distilled off, and the oxamates are saponified by heating with slaked lime. The calcium oxamates can be separated by crystallisation, the di*iso*butyloxamate being the more soluble in alcohol, from which it separates in slender silky needles (Malbot, Compt. rend. 104, 928).

Can be produced by hea[t] *iso*butyl alcohol with ammoniacal zinc chl[oride] 260° (Merz and Gasiorowski, Ber. 17, [627]). [The] action of caustic potash (10 p.c.) [on a] mixture of bromine and *iso*val[eric] [ac]ids at 60° (Hofmann, Ber.

Mixed with water, contraction [and] development of heat are produced. A mixture of equal volumes of water and *iso*butylamine has a sp.gr. of 0·9002 at 15°/15°, instead of the calc. density 0·8681 (Perkin, Chem. Soc. Trans. 1889, 696). With absolute alcohol and the amine similar results were obtained, the sp.gr. of a mixture of equal volumes being 0·791 at 15°/15°, instead of 0·7652, the calculated number.

(*c*) *Secondary butylamine*

$$C_2H_5{\cdot}CH(NH_2){\cdot}CH_3;$$

b.p. 63°; sp.gr. 0·718 at 23° (Menschutkin, Chem. Zentr. 1898, i. 702). Formed by the action of potash upon secondary butyl cyanate, or of ammonia upon secondary butyl iodide (Hofmann, Ber. 7, 513). Also by the action of dilute sulphuric acid upon secondary butyl mustard oil (Reymann, Ber. 7, 1289).

By the reduction of methyl ethyl ketoxime by hydrogen and finely divided nickel at 160°–170°, secondary butylamine and di-secondary butylamine are produced. They are liquids, the latter boiling at 132°/758 mm. and forming an oxalate melting at 104° (Mailhe, Compt. rend. 1905, 113).

Secondary butylamine has been separated into its optical antipodes by Thomé (Ber. 1903, 582); $[\alpha]_D$ 7·42° at 20°.

(*d*) *Tertiary butylamine* $(CH_3)_3C{\cdot}NH_2$; b.p. 45·2° at 760 mm. (Rudnew, Chem. Soc. Abstr. 1879, 40, 141); 43·8° at 760 mm.; sp. gr. 0·7137 at 3°, 0·7054 at 8°, 0·6931 at 15° (R.). Formed in small quantity by the action of potash upon *iso*butyl cyanate (Linnemann, Annalen, 162, 19; Hofmann, Ber. 7, 513). Also as a by-product in preparing trimethyl acetic acid from trimethyl carbinol iodide and mercuric cyanide (Rudnew).

2. **Dibutylamines.**

(*a*) *Di-normal butylamine*

$$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)_2NH;$$

b.p. 160°. Formed in small quantities by the action of potash upon butyl cyanate (Lieben and Rossi, Annalen, 158, 175); also by the action of butyl chloride on ammonia (Berg, Ann. Chim. Phys. [7], 3, 294). Gives $[(C_4H_9)_2NH{\cdot}HCl]_2PtCl_4$; yellow needles, almost insoluble in cold water.

(*b*) *Di-iso-butylamine*

$$[(CH_3)_2CH{\cdot}CH_2]_2NH;$$

b.p. 135°–137°; sp.gr. 0·7577 at 4°/4°, 0·7491 at 15°/15°, 0·7425 at 25°/25° (Perkin, Chem. Soc. Trans. 1889, 697). From *iso*butyl bromide and alcoholic ammonia at 150° (Ladenburg, Ber. 12, 949); also from *iso*butyl alcohol and ammoniacal zinc chloride at 270° (Merz and Gasiorowski, Ber. 17, 627). The hydrochloride $(C_4H_9)_2NH{\cdot}HCl$ forms plates or leaflets easily soluble in alcohol and water, slightly in ether. The platinum compound forms dark-red prisms, soluble in water, alcohol, and ether (Malbot, Compt. rend. 104, 366). The nitroso- derivative $(C_4H_9)_2N{\cdot}NO$ is a disagreeably smelling oil; m.p. 0°; b.p. 213°–216° (with decomposition); obtained by the action of potassium nitrite upon the hydrochloride (Ladenburg, Ber. 12, 949).

(*c*) *Di-tertiary butylamine*

$$[(CH_3)_3C]_2NH;$$

produced as iodide when tertiary butyl iodide and tertiary butylamine are heated to 50°; at 70° the mixture is decomposed, forming isobutylene and tertiary butylammonium iodide (Rudnew). The iodide is easily soluble in water or alcohol; on heating the aqueous solution evolves tertiary butylamine.

3. **Tributylamines.**

(*a*) *Tri-normal butylamine* $(C_4H_9)_3N$; b.p. 211°–215° at 740 mm.; sp.gr. 0·791 at 0°, 0·7782 at 20°, 0·7677 at 40°. From butyl cyanate and potash, together with the mono- and di- compounds (Lieben and Rossi, Annalen, 165, 115). With butyl iodide forms iodide of tetrabutylammonium $N(C_4H_9)_4I$, which crystallises in small plates (L. and R.). Also by the action of ammonia on butylchloride; b.p. 216·5° (Berg. Ann. Chim. Phys. [7] 3, 299).

(*b*) *Tri-iso-butylamine* $(C_4H_9)_3N$; b.p. 177°–180° (Reimer, Ber. 3, 757); 184°–186° (Sachtleben, Ber. 11, 733). Sp.gr. 0·785 at 21° (S.). From di*iso*butylamine and *iso*butyl bromide

(R.). From the alcohol and ammoniacal zinc chloride at 270° (Merz and Gasiorowski, Ber. 17, 627); also from *iso*butyl iodide and aqueous ammonia at 160° (Malbot, Compt. rend. 105, 574). Is not miscible with water. Forms salts with hydrochloric, nitric, and sulphuric acids, which are extremely soluble and crystallise with difficulty. The platinum double salt forms large ruby-red crystals (Malbot, Compt. rend. 104, 366).

Butylenes C_4H_8. Three isomeric butylenes are possible and all are known.

1. *Normal* (*α*)-*butylene*. *Ethyl ethylene* $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$; b.p. −5°.

Formation.—From normal butyl iodide and alcoholic potash (Saytzeff, J. pr. Chem. [2] 3, 88; Grabowsky and Saytzeff, Annalen, 179, 330). From bromethylene and zinc-ethyl (Wurtz, Annalen, 152, 21), together with butyl alcohol. From normal butylamine and nitrous acid (V. Meyer, Ber. 10, 136). Prepared by digesting on the water-bath 100 grams normal butyl iodide, 200 grams potash, and 150 grams alcohol (90 p.c.) (S.). A gas at ordinary temperatures, which combines readily with hydriodic acid to form secondary butyl iodide; and with hypochlorous acid to form chloromethylethyl carbinol $CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$.

2. *β-Butylene*. *Symmetrical dimethylethylene* $CH_3{\cdot}CH{:}CH{\cdot}CH_3$; b.p. 1° at 741·4 mm. (Lieben, Annalen, 150, 108); sp.gr. 0·635 at −13·5 (Puchot, Bull. Soc. chim. 30, 188).

Formed by the action of potash upon secondary butyl iodide (Luynes, Annalen, 129, 200; Lieben, *ibid.* 150, 108). Together with *iso*butylene by dropping *iso*- or normal butyl alcohol upon strongly heated zinc chloride (Nevole, Bull. Soc. chim. 24, 122; Le Bel and Greene, Amer. Chem. J. 2, 23). From trithioaldehyde $(C_2H_4S)_3$ and copper (Eltekow, Ber. 10, 1904). By heating a mixture of methyl iodide and allyl iodide with sodium (Wurtz, Annalen, 144, 235).

Preparation.—*Iso*butyl alcohol is allowed to drop upon heated zinc chloride, and the evolved gas is led into sulphuric acid diluted with half its volume of water; this retains the *iso*butylene. The unabsorbed gas is led into bromine, and is again liberated by action of sodium (Le Bel and Greene, Bull. Soc. chim. 29, 306). Two stereoisomeric modifications are known (Wislicenus, Chem. Zentr. 1897, ii. 267).

β-Butylene combines with bromine to form a dibromide boiling at 156°–158°. This compound, by the action of potash, forms mono-bromo-pseudo-butylene $CH_2{\cdot}CBr{:}CH{\cdot}CH_3$; b.p. 87°–88° (Hölz, Annalen, 250, 230). Chlorine forms a dichloride; b.p. 112°–114° (Chechoukow, Bull. Soc. chim. 43, 127).

3. *γ-Butylene*. *Iso*butylene, *unsymmetrical dimethyl ethylene* $(CH_3)_2C{:}CH_2$; b.p. −6° (Butlerow, Zeitsch. Chem. 1870, 236). Liquefied by a pressure of 2–2½ atmospheres at 15°–18°. Is produced by the dry distillation of fats (Faraday, Phil. Trans. 1825, 440); by heating the vapour of fusel oil to redness (Wurtz, Annalen, 104, 249), together with ethylene and ethane; also from light petroleum, 'ligroin' (b.p. 60°–90°) (Prunier, J. 1873, 347); from *iso*- or tertiary-butyl iodide and alcoholic potash (Butlerow, Annalen, 144, 19); by heating trimethyl carbinol and dilute sulphuric acid (1 vol. H_2SO_4 to 2 vols. water) (Butlerow); from *iso*butyl alcohol and zinc chloride, though in very small quantity (Nevole, Bull. Soc. chim. 24, 122).

Preparation.—(1) 5 parts of *iso*butyl alcohol, 5 parts sulphuric acid, 1 part of water and sand are heated together (Lermontow, Annalen, 196, 117). (2) Puchot's method (Ann. Chim. Phys. [5] 28, 508) of heating *iso*butyl alcohol with a mixture of sulphuric acid, potassium sulphate, and gypsum, gives a mixture of pseudo- and *iso*-butylene. (3) A mixture of 2 parts of caustic potash and 3 parts of alcohol (90 p.c.) is slowly added to 2 parts of *iso*butyl iodide, and gently warmed (Butlerow, Zeitsch. f. chem. 1870, 238). Butylene is a gas, with unpleasant smell, slightly soluble in water; combines with hydriodic acid to form tertiary butyl iodide. A mixture of three parts of sulphuric acid and 1 part of water completely absorbs the gas; on distilling the diluted solution trimethyl carbinol is evolved. It forms a mercury compound $C_4H_8(HgNO_3)(Hg_2NO_3)$ (Denigès, Compt. rend. 126, 1043). Oxidising agents—*e.g.* potassium permanganate—form carbon dioxide, formic and acetic acids, and oxalic acid (and in the case of chromium trioxide, acetone) (Zeidler, Annalen, 197, 251). By the action of a mixture of 5 parts sulphuric acid and 1 part of water forms dodecylene (tri*iso*butylene) $C_{12}H_{24}$; b.p. 177·5°–178·5°; sp.gr. 0·774 at 0° (Butlerow, Ber. 6, 561).

Butylene alcohol *v. Butylene glycols.*

Butylene dibromides.

1. *Normal butylene dibromide*, *αβ-dibrombutane* $CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$; b.p. 165·6°–166°; sp.gr. 1·876 at 0° (Wurtz, Annalen, 152, 23), 1·8503 at 0°, 1·8204 at 20°/0° (Grabowsky and Saytzeff, Annalen, 179, 332). Formed from *α*-butylene and bromine (Wurtz); from normal buty bromide and bromine at 150° (Linnemann, Annalen 161, 199). Gives *α*-butylene by action of sodium.

2. *β-Butylene dibromide*, *βγ-dibrombutane* $CH_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$; b.p. 158°; sp.gr. 1·821 at 0°. Formed from *β*-butylene and bromine (Wurtz, Annalen, 144, 236), or by heating *α*- or *β*-brombutane with iron and bromine (V. Meyer and Muller, J. pr. Chem. [2] 46, 180). Decomposed by heating to 140° with water and lead oxide, forming lead bromide and methyl ethyl ketone (Eltekow, Chem. Soc. Abstr. 1879, 34).

3. *Iso-butylene di-bromide*, *αβ-dibrom-β-methyl propane* $(CH_3)_2CBr{\cdot}CH_2Br$; b.p. 148°–149° at 737 mm.; sp.gr. 1·798 at 14° (Linnemann, Annalen, 162, 36). From *iso*-butylene and bromine (L.; also Wurtz, Annalen, 104, 249; Hell and Rothberg, Ber. 22, 1737). By heating with water to 150° *iso*butyraldehyde and *iso*butylene glycol are formed.

4. *Tetramethylenedibromide*, *αδ-dibrombutane*, $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Br$.; boils at 188°–190° (Gustavson and Demjanoff, J. pr. Chem. [2] 39, 543). (*See* also Haincourt, Compt. rend. 132, 345.)

5. *ββ-Dibrombutane* $CH_3{\cdot}CBr_2{\cdot}CH_2{\cdot}CH_3$; boils at 144°–145° (Wislicenus and Holz, Annalen, 250, 232).

6. *αγ-Dibrombutane*

$CH_2Br{\cdot}CH_2{\cdot}CH_2Br{\cdot}CH_3$;

boils at 174°–175° (Perkin, Chem. Soc. Trans. 1894, 963).

Butylene cyanide.

Isobutylene dicyanide (*dimethyl succinonitrile*) $CN{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CN$; b.p. 218°–220°. By treating an aqueous alcoholic solution of potassium cyanide with γ-butylene bromide, and allowing the mixture to stand for a fortnight. A colourless oil, moderately soluble in water. Heated to 150° with strong hydrochloric acid, it is decomposed into ammonia and dimethylsuccinic acid (Hell and Rothberg, Ber. 22, 1737).

Butylene glycolchlorhydrin, β-chloro*iso*butyl-alcohol $(CH_3)_2{\cdot}CCl{\cdot}CH_2OH$; b.p. 137. From *iso*butylene and hypochlorous acid (Butlerow, Annalen, 144, 25). Soluble in large excess of water. See also Michael and Leighton (Ber. 1906, 2157).

β-Chloro*iso*butyl alcohol is also formed by the union of hydrogen chloride with *iso*butylene oxide, which results from the action of dry powdered potassium hydroxide on chlorotrimethyl carbinol. The last may be prepared from magnesium methyl bromide, chloroacetone and ethyl chloroacetate. β-chloro*iso*butyl alcohol boils at 132°–133°. It forms a nitrate by the action of concentrated sulphuric and nitric acids $C(Me)_2Cl{\cdot}CH_2NO_3$, and a nitrite $C(Me)_2Cl{\cdot}CH_2NO_2$ with nitrous acid, which distinguishes it from the isomeric chlorotrimethyl carbinol (L. Henry, Compt. rend. 1906, 142, 493).

Butylene diamines.

1. *Tetramethylenediamine* (*putrescine*), αδ-diaminobutane $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, occurs in urine and fæces in cases of cystinuria, and also arises during the putrefaction of herrings. It is prepared by reducing an alcoholic solution of dicyanoethylene with sodium (Ladenburg, Ber. 1886, 780; Lellmann and Winthaer, Annalen, 228, 229); or in a similar manner from succinaldehyde dioxime (Ciamician and Zanetti, Ber. 1889, 22, 1968, 1970). Colourless crystals melting at 27°–28° (C. Z.) and boiling at 158°–160°. Smells like piperidine. It is strongly basic, readily absorbs CO_2, and forms a well-defined dihydrochloride, aurichloride, and platinichloride. The picrolonate is of some physiological importance (Otori, Chem. Soc. Abstr. 1905, ii. 126).

Willstätter and Heubner have prepared the tetramethyl derivative of tetramethylene diamine, and the biquaternary hexamethylammonium salt corresponding to it (Ber. 1907, 3871, 3874). The identity of αδ-diaminobutane with putrescine rests on the experiments of Udranszky and Baumann (Ber. 1888, 2938). Brieger (Chem. Zentr. 1907, i. 1703) considers the identity not proven, as also do Willstätter and Heubner (*l.c.*).

2. *Dimethylethylenediamine*, βγ-*diaminobutane* $CH_3{\cdot}CHNH_2{\cdot}CHNH_2{\cdot}CH_3$, has been prepared by Angeli (Ber. 1890, 1358).

Iso-**Butylacetic acid** *v.* CAPROIC ACID.

Butyl chloral *v.* CHLORAL.

Butyl-lactinic acid *v.* HYDROXYBUTYRIC ACIDS.

Butylene glycols.

1. *Normal-(α)-butylene glycol*, αβ-*dihydroxybutane* $CH_3{\cdot}CH_2{\cdot}CHOH{\cdot}CH_2OH$; b.p. 191°–192° at 747·1 mm.; sp.gr. 1·0189 at 0°/0°, 1·0059 at 17·5/0°. From normal butylene dibromide (Saytzeff and Grabowsky, Annalen, 179, 332).

2. *β-Butylene glycol*, αγ-*dihydroxybutane* $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2OH$; b.p. 203·5°–204° (Kekulé, Annalen, 162, 310); sp.gr. 1·0259 (Wurtz, J. 1873, 474; Bull. Soc. chim. 41, 362). Produced in small quantity by the reduction of dilute aqueous solution of aldehyde by sodium-amalgam (K.). Prepared from β-oxybutyric aldehyde by reduction with sodium amalgam (W.).

3. *Isobutylene glycol*, αβ-*dihydroxy-α-methylpropane* $(CH_3)_2C(OH){\cdot}CH_2OH$; b.p. 176°–178°; sp.gr. 1·0129 at 0°, 1·003 at 20°. Produced by the fermentation of sugar in presence of tartaric acid (Henninger and Sanson, Compt. rend. 106, 208). Formed by heating *iso*butylene bromide with potassium carbonate and water (Nevole, Bull. Soc. chim. 27, 63); also by oxidation of *iso*butylene by means of potassium permanganate in neutral aqueous solution (Wagner, Ber. 21, 1232).

4. *Symmetrical dimethylethylene glycol*, βγ-*dihydroxybutane* $CH_3{\cdot}CHOH{\cdot}CHOH{\cdot}CH_3$; b.p. 183°–184°. Formed by heating for 6 or 7 hours 1 vol. of symmetrical dimethylethylene oxide C_4H_8O with 3 vols. of water to 100° (Eltekow, Chem. Soc. Abstr. 1883, 566).

5. *Tetramethylene glycol*, αδ-*dihydroxybutane* $OH{\cdot}(CH_2)_4{\cdot}OH$; boils at 203°–205°; sp.gr. 1·0111 (Dekkers, Chem. Soc. Abstr., 1891, 164).

6. *A-butylene glycol*, differing from the above, boiling at 183°–184°; has also been prepared by Wurtz (Ann. Chim. Phys. [3] 55, 452); sp.gr. 1·048 at 0°.

7. *α-Methyl propanediol*

$OH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2OH$

(Henry, Bull. Soc. chim. [3] 13, 1002 Cesaro, Chem. Zentr. 1897, ii. 179).

Butylene diiodide, αγ-*diiodobutane*

$CH_3{\cdot}CHI{\cdot}CH_2{\cdot}CH_2I$;

sp.gr. 2·291. From β-butylene glycol and hydriodic acid (Wurtz, Bull. Soc. chim. 41, 362).

Isobutylene dinitrite $C_4H_8(NO_2)_2$. By treatment of *iso*butylene with concentrated nitric acid (Haitinger, Monatsh. 2, 287). Forms a crystalline mass. Probably the same body was obtained by Beilstein and Kurbatow (Ber. 14, 1621) by treating the petroleum of Tiflis (b.p. 40°–50°) with nitric acid (sp.gr. 1·52). It formed needles which melted at 96°. They were insoluble in water, but soluble in alcohol and ether.

Butylene oxides C_4H_8O.

1. *Isobutylene oxide* $(CH_3)_2C{<}\begin{matrix}O\\ \\ CH_2\end{matrix}$; b.p. 51°–52°; sp.gr. 0·8311 at 0°. From the chlorhydrin C_4H_9ClO, and potash (Eltekow, Chem. Soc. Abstr. 1883, 566).

2. *s-Dimethylethylene oxide*

b.p. 56°–57°; sp.gr. 0·8344 at 0°. Formed from the chlorhydrin (prepared from the symmetrical dimethyethylene and hypochlorous acid) and potash (Eltekow, Chem. Soc. Abstr. 1883, 566).

BUTYRALDEHYDE. *Butyric aldehyde* C_4H_8O. This compound exists in two isomeric forms, termed normal and *iso*butyric aldehyde respectively.

Normal butyraldehyde $CH_3{\cdot}(CH_2)_2{\cdot}CHO$ is formed together with acetaldehyde and propaldehyde by the action of chromic acid upon fibrin, casein, and albumen (Guckelberger, Annalen, 64, 39). It is readily prepared by distilling a mixture of calcium formate (2 mols.) and

calcium butyrate (1 mol.) in quantities of 50 grams at a time with twice the weight of iron filings. The distillate is fractionated, the fraction 70°–110° treated with sodium hydrogen sulphite (bisulphite), then shaken with ether to extract impurities, and finally distilled with excess of soda (Lipp, Annalen, 211, 355; Linnemann, *ibid.* 161, 186; Kahn, Ber. 1885, 3364). Bodroux has applied Grignard's reagent to a solution of orthoformic and acetaldehyde, thereby obtaining a 75 p.c. yield of butyraldehyde (Chem. Zentr. 1904, i. 1077).

Properties.—Normal butyraldehyde is a liquid which boils at 73°–74° (Lipp, at 73°–77°) and has a sp.gr. 0·8170 at 20°/4° (Brühl, Annalen, 203, 18). It is soluble in 27 parts of water. With sodium hydrogen sulphite (bisulphite) it unites, yielding a crystalline compound (Justin, Ber. 1884, 2505). When treated with aqueous ammonia at 0°, it yields butyraldehyde-ammonia $C_4H_{11}NO,3\frac{1}{2}H_2O$, which crystallises in acute rhombic tetrahedra and melts at 30°–31° (Guckelberger). If, however, alcoholic ammonia and the aldehyde are allowed to stand for a month, and then heated for a day at 100°, condensation occurs, and, after removal of ammonia, alcohol and unattacked butyraldehyde by distillation, two bases, tetrabutyraldine and dibutyraldine $C_8H_{17}NO$ can be separated by fractional precipitation with platinic chloride. The latter only can be crystallised, and when heated is converted into paraconine $C_8H_{15}N$ and water (Schiff, Annalen, 157, 352). The trichlorobutyraldehyde (butylchloral) and its hydrate have been prepared by Pinner (Annalen, 179, 26).

***Iso*butyraldehyde** $(CH_3)_2CH\cdot CHO$ can be prepared by the oxidation of *iso*butyl alcohol with potassium dichromate and sulphuric acid (Lipp, Annalen, 205, 2; Pinner, Ber. 5, 699; Fossek, Monatsh. 2, 614; 4, 661), or by distilling calcium formate with calcium *iso*butyrate (Linnemann and Zotta, Annalen, 162, 7). It dissolves in 9 parts of water at 20°, and is soluble in alcohol and ether. The boiling-point is 63°–64° at 757 mm. (Brühl, Annalen, 203, 18), and the sp.gr. 0·7938 at 20°/4° (Brühl), 0·79722 at 15° (Perkin, Chem. Soc. Trans. 1884, 476). Condensation compounds have been obtained by Perkin (Chem. Soc. Trans. 1883, 91).

BUTYRIC ACID $C_4H_8O_2$. Two isomeric forms of this acid are known, normal butyric and *iso*butyric acid.

Normal butyric acid $CH_3\cdot CH_2\cdot CH_2\cdot COOH$.

Occurrence.—In ordinary butter in combination with glycerol to the extent of 2 p.c.; also in the fruits of *Heracleum villosum* (Fisch) and of *Peucedanum sativum* (Benth. Cl. Hook, *f.*) as hexyl butyrate and octyl butyrate respectively. Butyric acid is also found in flesh juice, and is frequently a constituent of decomposing organic matter (*v.* art. FERMENTATION) (J. 1857, 353, 402, 403, 559; 1858, 231; 1859, 363, 364; 1861, 454; 1866, 311). The occurrence of butyric acid in sour milk is treated of by Thorpe (Chem. Zentr. 1909, ii. 1774).

Preparation.—(1) Butyric acid is a frequent product of the oxidation of organic substances; casein, fibrin, and albumen, for example, yield this acid among other products on oxidation with manganese dioxide and sulphuric acid (Guckelberger, Annalen, 64, 68).

(2) All amylaceous and saccharine substances which yield lactic acid as a product of their fermentation can undergo a further fermentation to butyric acid, and this fact is made use of for the preparation of the acid. 5 kilos. of rice or potato starch are boiled with 60 litres of water for some hours, allowed to cool, and the product after 24 hours is treated with 60 grams of malt stirred up with 2 litres of milk, with 1 kilo. of finely divided flesh, and with 2 kilos. of chalk, the chalk being added to neutralise the lactic and butyric acids as rapidly as they are formed, and the whole is allowed to remain with occasional stirring for several weeks at a temperature of 25°–30°. When the evolution of gas has ceased, the product is heated to 80°, filtered, precipitated with sodium carbonate to decompose the calcium salt, again filtered, evaporated to a small bulk, and treated with sulphuric acid. The oily layer of acid so obtained is fractionated to free it from the acetic and caproic acids formed simultaneously, and the fraction 155°–174° is extracted with water, which dissolves the butyric acid but leaves the caproic acid undissolved; the aqueous extract is then neutralised with lime, the solution concentrated, and the salt finally decomposed by hydrochloric acid (Grillone, Annalen, 165, 127).

(3) In the presence of a schizomyces—the so-called *Bacillus subtilis*, which can readily be obtained by stirring hay in water, straining the liquor through a sieve, and boiling for 5 minutes—Fitz (Ber. 11, 52) has found that starch readily undergoes fermentation, yielding normal butyric acid as chief product.

Butyric acid has also been obtained by the fermentation of glycerol in 3 p.c. aqueous solution with a species of schizomyces (Fitz, Ber. 9, 1348; 10, 276), and has been prepared by various synthetical methods (Frankland and Duppa, Annalen, 138, 218; Geuther and Frölich, *ibid.* 202, 306). (For conditions affecting the production of butyric acid by fermentation, see FERMENTATION.)

Properties.—Butyric acid is a colourless, transparent liquid, having an odour resembling that of rancid butter, and a sour burning taste. Cooled to −19° it solidifies, and the crystals melt at about −2°. The acid boils at 161·5° at 760 mm. (Kahlbaum, Ber. 16, 2480); at 162·3° (corr.) (Linnemann, Annalen, 160, 228; Zander, *ibid.* 224, 64); and has a sp.gr. 0·96704 at 15°/15° (Perkin, Chem. Soc. Trans. 1884, 483), 0·9590 at 20°/4°; μ_D, 1·39906 (Scheig, R. 1899, 169). Butyric acid is inflammable and burns with a blue flame. Alcohol, wood-spirit, and water dissolve it in all proportions, and from the aqueous solution it can be separated by addition of calcium chloride. Prolonged boiling with nitric acid converts it into succinic acid. By the action of calcium carbide, dipropyl ketone may be obtained (Haehn, Chem. Zentr. 1906, ii. 17).

Salts.—The metallic salts of normal butyric acid are generally soluble in water, and are crystalline. $NaC_4H_7O_2$ and $KC_4H_7O_2$ crystallise in indistinct cauliflower-like groups. $AgC_4H_7O_2$ crystallises in needles or monoclinic prisms, and dissolves in 200 parts of water at 14° (Linnemann and Zotta, Annalen, 161, 177); 100 parts of water dissolve 0·413 part at 16° (Grünzweig, Annalen, 162, 203). $Mg(C_4H_7O_2)_2,5H_2O$ crystallises in very soluble scales (Pelouze and Gélis, Annalen, 47

249). $Ba\bar{B}_2,4H_2O$ crystallises in nacreous scales, and dissolves in 2·48 parts of water at 14° (Linnemann and Zotta). $Ca\bar{B}_2,H_2O$ crystallises in rhombic forms; 100 parts of water dissolve 19·4 parts at 0°. (For solubility table, *see* Hecht, Annalen, 213, 72.) SiB_2 forms monoclinic prisms; 100 parts of water at 20° dissolve 39·2 parts of the salt (Grünzweig). $Zn\bar{B}_2,2H_2O$ forms monoclinic prisms; 100 parts of water at 16° dissolve 10·7 parts of the crystallised salt (Grünzweig). $Pb\bar{B}_2$ is an oil which slowly solidifies (Markownikow, Annalen, 138, 361). $Cu\bar{B}_2,H_2O$ crystallises in triclinic forms (Alth, Annalen, 91, 176), and $Cu\bar{B}_2,2H_2O$ crystallises in monoclinic forms (Pelouze and Gélis).

Separation from formic, acetic, and propionic acids.—Mach and Portele (Chem. Soc. Abstr. 1890, 1344) give the following method for the estimation of butyric acid in the presence of acetic acid (as in wine): 500 c.c. of the solution is distilled to a bulk of 125 c.c., diluted to the original volume, and again distilled till only 125 c.c. remains. This is done four times. The total acid in the distillate is estimated by titration with soda or baryta. If soda is used, the neutralised distillate is evaporated down, sulphuric acid is added, and the mixture steam-distilled. The distillate is neutralised with baryta and evaporated so far that it will solidify when cold. The barium butyrate is then extracted with absolute alcohol, and the aqueous solutions of the separated salts treated with sulphuric acid and steam-distilled, the acid in the distillate being subsequently titrated.

The separation of formic, acetic, propionic and butyric acids is also dealt with by Willcox (Chem. Soc. Proc. 1895, 202); Luck (Zeitsch. Anal. Chem. 10, 185); Haberland (*ibid.* 1899, 217); and Muspratt (J. Soc. Chem. Ind. 1900, 204). An expression connecting the percentage of butyric acid in an aqueous distillate with the proportion of the distillate to the original solution is given by Leonard, Smith, and Richmond (Analyst, 1897, 92).

Butyryl chloride, obtained by treating 96 grams of butyric acid with 100 grams of phosphorus trichloride (Burcker, Ann. Chim. Phys. [5] 26, 468); boils at 100°–101·5° (Linnemann); and has a sp.gr. 1·0277 at 23°/4° (Brühl).

Butyric anhydride, prepared by the action of butyryl chloride on butyric acid (Linnemann, Annalen, 161, 179), or by the action of 1 molecule of acetic anhydride or 2 mols. sodium butyrate (Michael, Chem. Zentr. 1901, i. 1088), boils at 191°–193° (L.); and has a sp.gr. 0·978 at 12·5° (Gerhardt, Annalen, 87, 156).

Butyramide, formed by heating dry ammonium butyrate for six hours at 230° (Hofmann, Ber. 1882, 982); crystallises in tables; melts at 115°; boils at 216° (J. 1856, 516); and is readily soluble in water.

α-Chlorobutyric acid $CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H$ is a thick liquid difficultly soluble in water (Markownikow, Annalen, 153, 241).

β-Chlorobutyric acid $CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$, thick liquid (Pinner, Ber. 1879, 2056; 1884, 2008).

γ-Chlorobutyric acid $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$. Esters only known (Henry, Chem. Zentr. 1898, ii. 273).

αβ-Dichlorobutyric acid $CH_3{\cdot}CHCl{\cdot}CHCl{\cdot}CO_2H$, melts at 72°–73° (Melikow, Annalen, 234, 201; 266, 372).

βγ-Dichlorobutyric acid $CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$; melts at 49°–50° (Léspieau, Compt. rend. 129, 225).

ααβ-Trichlorobutyric acid $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CO_2H$; melts at 60° (Kahlbaum Ber. 1879, 2337; Gargarolli, Annalen, 182, 185).

ααγ-Trichlorobutyric acid $CH_2Cl{\cdot}CH_2{\cdot}CCl_2{\cdot}CO_2H$; melts at 73°–75° (Natterer, Monatsh. 4, 551; 5, 256).

αββ-Trichlorobutyric acid $CH_3{\cdot}CCl_2{\cdot}CHCl{\cdot}CO_2H$; melts at 52° (Szenic and Taggesell, Ber. 1895, 2665).

Tetrachlorobutyric acid $C_4H_4Cl_4O_2$; melts at 140° (Pelouze and Gélis, Arch. Pharm. [3] 10, 434).

Bromobutyric acids have also been obtained by Naumann (Annalen, 119, 120), Schneider (J. 1861, 458), and Michael and Norton (Amer. Chem. J. 2, 16). (*See* also Cloves, Chem. Zentr. 1902, I. 406.)

***Iso*butyric acid** $(CH_3)_2{\cdot}CH{\cdot}COOH$.

Occurrence.—*Iso*butyric acid occurs in the fruit of *Siliqua dulcis* (Grünzweig, Chem. Soc. Trans. 1873, 373), and in arnica root (*Arnica montana*) (Sigel, Annalen, 170, 348).

Preparation.—*Iso*butyric acid is most readily prepared by the oxidation of *iso*butyl alcohol with a mixture of sulphuric acid and potassium dichromate. Pierre and Puchot (Ann. Chim. Phys. [4] 28, 366) give the following proportions: *Iso*butyl alcohol (300 parts) is mixed with water (1500 parts) and sulphuric acid (540 parts) and into the well-cooled mixture finely powdered potassium dichromate (400 parts) is gradually introduced. An ethereal layer separates, consisting of *iso*butyl *iso*butyrate, which is decomposed by allowing 55 parts to fall slowly on 100 parts of caustic potash to which one-tenth its weight of water has been added; the resulting potassium salt is then distilled with dilute sulphuric acid, and the aqueous acid purified by fractional distillation.

Synthetical methods for preparing this acid have been described by Frankland and Duppa (Annalen, 138, 337), and Markownikow (Annalen, 138, 361).

Properties.—*Iso*butyric acid resembles its isomeride in appearance, but has a less disagreeable odour. It boils at 152° at 760 mm. (Kahlbaum, Ber. 16, 2480); at 153·5°–153·8° at 750·3 mm. (Brühl, Annalen, 200, 180); at 154°–154·2° (Zander, *ibid.* 224, 77); sp.gr. 0·9651 at 0° (Zander); 0·9503 at 20° (Linnemann, Annalen, 162, 9). It dissolves in five times its volume of water (L.). The metallic salts of *iso*butyric acid are more soluble in water than those of the normal acid. The potassium and sodium salts form cauliflower-like masses. $Ag\bar{B}$ crystallises in characteristic tabular forms; 100 parts of water dissolve 0·928 part at 16° (Grünzweig, Annalen, 162, 210). $Mg\bar{B}_2$ forms white scales. $Ca\bar{B}_2,5H_2O$ forms four-sided monoclinic crystals; 100 parts of water at 18° dissolve 36 parts of crystallised salt (G.), and the solubility increases as the temperature rises. $Sr\bar{B}_2,5H_2O$; 100 parts of water at 17° dissolve 44·1 parts of the crystallised salt (G.). $Ba\bar{B}_2,\frac{1}{2}H_2O$ forms monoclinic crystals (Fitz, Ber. 1880, 1316).

ZnB_2,H_2O; 100 parts of water at 19·5° dissolve 17·3 parts of the crystallised salt (Grünzweig). PbB_2 crystallises in rhombic tables and dissolves in 11 parts of water at 16°.

***Iso*butyryl chloride**, prepared by treating *iso*butyric acid (12 parts) with phosphorus trichloride (7 parts), and subsequently distilling (Tönnies and Staub, Ber. 1884, 850); boils at 91·5°–92·5° at 748·2 mm.; and has a sp.gr. 1·0174 at 20°/4° (Brühl, Annalen, 203, 20).

***Iso*butyryl anhydride**, obtained by boiling *iso*butyric acid with *iso*butyryl chloride for 12 hours in a reflux apparatus and fractionating the product (Tönnies and Staub, Ber. 1884, 850); boils at 181·5° at 734 mm.; and has a sp.gr. 0·9574 at 16·5°.

***Iso*butyramide**, formed by heating dry ammonium *iso*butyrate at 230° for six hours; melts at 128°–129° (Hofmann, Ber. 1882, 982).

α-Chloro*iso*butyric acid $(CH_3)_2CCl\cdot CO_2H$; melts at 31° and boils at 118° (Henry, Bull. Soc. chim. 26, 24; Balbiano, Ber. 1878, 1693).

αβ-Dichloro*iso*butyric acid
$CH_3\cdot CH(CH_2Cl)\cdot CCl\cdot CO_2H$ (Brochet, Ann. Chim. Phys. [7] 10, 375).

Trichloro*iso*butyric acid $C_4H_5Cl_3O_2$; melts at 50° (Gottlieb, J. pr. Chem. [2] 12, 1).

Bromo*iso*butyric acids have been prepared by Markownikow (Annalen, 153, 229); Engelhorn (*ibid.* 200, 65, 68); Cahours (*ibid.* Supplt. 2, 349, 352).

Butyric esters. These compounds are for the most part prepared by the action of butyric acid on the corresponding alcohols in presence of some dehydrating agent such as sulphuric acid, the temperature being raised eventually to complete the reaction. Butyric esters are liquids which dissolve in alcohol and ether in all proportions, but are only very sparingly soluble in water. On saponification with caustic potash they yield the corresponding alcohol and potassium butyrate.

Methyl butyrate $C_4H_7O_2Me$, prepared similarly to the ethyl ester, is a colourless liquid with a pleasant odour resembling that of pine-apples. It boils at 102·3° at 760 mm. (Schumann, Pogg. Ann. [2] 12, 41); and has a sp.gr. 0·9194 at 0°/4° (Elsässer, Annalen, 218, 314).

Ethyl butyrate, *butyric ether*, is prepared by adding 1 part by weight of sulphuric acid to 2 parts each by weight of butyric acid and alcohol. The liquid becomes heated, and the mixture at once separates into two layers of which the upper one consists of ethyl butyrate. To complete the reaction it is necessary to heat the product at about 80° for a short time. The upper layer is separated, washed with water, dried over calcium chloride, and distilled. The presence of considerable quantities of water does not seem to hinder esterification (Pelouze and Gélis, Annalen, 47, 250).

Ethyl butyrate is a colourless liquid having an odour like that of pine-apples. It boils at 119·9° at 760 mm. (Schumann); and has a sp.gr. 0·8996 at 0°/4° (Elsässer). A solution of ethyl butyrate is used in perfumery and in confectionery under the name of pine-apple oil.

Propyl butyrate boils at 142·7° at 760 mm. (Schumann); and has a sp.gr. 0·8930 at 0°/4° (Elsässer).

***Iso*propyl butyrate** boils at 129° at 755 mm.; and has a sp.gr. 0·8787 at 0° (Silva, Ber. 1869, 283), 0·9027 at 0° (Přibram and Handl, Monatsh. 2, 690).

Butyl butyrate boils at 164·8° (corr.), and has a sp.gr. 0·8760 at 12° (Linnemann, Annalen, 161, 195; compare also Lieben and Rossi, *ibid.* 158, 170).

***Iso*butyl butyrate** boils at 156·9° at 760 mm. (Schumann); and has a sp.gr. 0·8798 at 0°, 0·8664 at 16° (Grünzweig, Annalen, 162, 207).

***Iso*amyl butyrate** boils at 178·6° at 760 mm. (Schumann); and has a sp.gr. 0·8823 at 0°/4° (Elsässer).

The hexyl- and octyl-butyrates occur in the oils from the fruits of *Heracleum giganteum* (Franchimont and Zincke, Ber. 4, 824) and *Pastinaca sativa* (Renesse, Annalen, 166, 80) respectively.

Ethereal salts of *iso*butyric acid have been prepared:

Methyl *iso*butyrate boils at 92·3° at 760 mm. (Schumann); and has a sp.gr. 0·9112 (Elsässer).

Ethyl *iso*butyrate boils at 110·1° at 760 mm. (Schumann); its sp.gr. is 0·8903 (Elsässer).

Propyl *iso*butyrate boils at 133·9° at 760 mm. (Schumann; its sp.gr. is 0·8843 (Elsässer).

***Iso*propyl isobutyrate** boils at 118°–121° at 727 mm.; and has a sp.gr. 0·8787 at 0° (Přibram and Handl).

***Iso*butyl *iso*butyrate** boils at 146·6° at 760 mm. (Schumann); its sp.gr. at 0° 0·8752 (Grünzweig).

***Iso*amyl *iso*butyrate** boils at 168·8° at 760 mm. (Schumann); and has a sp.gr. 0·8759 at 0°/4° (Elsässer).

BUTYROLACTONE *v.* HYDROXYBUTYRIC ACIDS.

BUTYRONE, *Dipropyl ketone* $C_7H_{14}O$.

Butyrone is obtained by distilling calcium butyrate, or preferably a mixture of calcium butyrate and calcium carbonate (Schmidt, Ber. 5, 597); the crude product is dehydrated by treatment with calcium chloride, and purified by fractional distillation. Butyrone boils at 144°, and has sp.gr. 0·8195 at 20°, does not combine with ammonia or sodium hydrogen sulphite (bisulphite), yields a mixture of propionic and butyric acids on oxidation with chromic acid, and is converted into a secondary alcohol $C_7H_{16}O$ and butyrone-pinacone $C_{14}H_{30}O_2$ on treatment with sodium amalgam and water (Kurtz, Annalen, 161, 205).

An isomeride ***di-isopropylketone*** can be prepared by distilling calcium *iso*butyrate (Münch, Annalen, 180, 327); it boils at 124°–126°, has a sp.gr. 0·8254 at 17°, and does not combine with sodium hydrogen sulphite.

BUTYRO-REFRACTOMETER *v.* REFRACTOMETERS.

BUXIN. An alkaloid obtained from the box-tree (*Buxus sempervirens*). Hager (Chem. Zentr. 1877, 119) found it in beer as an adulterant. It is said by Walz (N. J. P. 14, 15) to be identical with bebeerine (*v.* VEGETO-ALKALOIDS).

C.

CABBAGE, *Brassica oleracea.* This plant has been modified by careful selection and cultivation so as to produce several apparently very different varieties:

1. Those which form a compact head by overlapping of the leaves, as in the ordinary cabbage.

2. Those of a straggling, open habit of growth, with a branching stem but no distinct 'heart' or head, *e.g.* thousand-headed kale.

3. Those in which a dense head of imperfect flowers are formed, as cauliflower and broccoli.

4. Those in which the stem is enormously developed so as to form a globe, as in kohl-rabi.

5. Those in which a large number of small 'heads' are formed on a tall stem—Brussels sprouts.

Of the cabbage itself, there are many varieties, differing in size, shape, and colour.

Like all the members of the *Cruciferæ*, cabbages contain sulphur compounds, some of which easily undergo decomposition with production of sulphuretted hydrogen.

The average composition of cabbages, as used for cattle food, is, according to Kellner—

Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
84·7	2·5	0·7	8·1	2·4	1·6

whilst, according to American analyses, the edible portion of culinary cabbages contains:

Water	Protein	Fat	Sol. carbohydrates Fibre	Ash
90·3	2·1	0·4	5·8	1·4

Cabbages, as a farm crop, respond to liberal manuring, and in inland districts are benefited by a small dressing of the soil with common salt. They do best, as a rule, on heavy land, and are usually transplanted from seed-beds. H. I.

CACAO BUTTER (spelt also Cocoa Butter), is expressed from the cacao bean, the seeds of the cacao tree, *Theobroma cacao* (Linn.).

The cacao tree is indigenous to the West Indies, but has been introduced into various tropical countries, especially Central and South America and to the West Coast of Africa and the islands in the Bay of Benin. It has also been introduced into Nigeria, and an inducement has been held out by the Government to the Nigerian peasants to grow cacao. As the beans are chiefly worked up for the preparation of cacao, the cacao butter must be considered, to some extent, a by-product of the chocolate industry. For the production of cacao butter, the beans are roasted over a coke fire, and the husks are separated by winnowing. The kernels thus laid bare are ground under millstones and reduced to a paste, when the bulk of the fat is removed by hot expression in hydraulic presses. As the fat in the bean has undergone slight hydrolysis, it is usual to add a carbonate, either of potassium or ammonium, to the beans before roasting. Hence, in the examination of cacao butter, the presence of ammonia or potash soap may be expected.

The average composition of the cacao bean is, according to König, as follows:—

	Per cent.
Fat	49·0
Water	5·4
Albuminoids	12·8
Carbohydrates	25·7
Crude fibre	3·71
Ash	3·41

The composition of the shell is as follows:—

Fat	4·21
Water	11·19
Albuminoids	13·61
Carbohydrates	43·95
Crude fibre	17·63
Ash	9·88
	100·47

The proportion of fat in the bean varies from 50 to 56 p.c. In the production of cacao powder, only a portion of the cacao butter is expressed, whereas the beans intended for the manufacture of *best* chocolate are not expressed, so that the full amount of fat is allowed to remain in the ground mass. Manufacturers of cheap chocolates remove a portion of the costly cacao butter by expression, replacing it by cheaper substitutes (*see* CHOCOLATE FATS). The kernels contain a small amount of theobromine, a portion of which passes into the cacao butter on expression.

Cacao butter has a yellowish-white colour, turning white on keeping, an agreeable taste and pleasant odour, recalling that of chocolate. At the ordinary temperature, the fat is somewhat brittle. It appears to consist, to a very large extent, of oleodistearin and oleodipalmitin. The solid acids of cacao butter consist of stearic and palmitic acids; small quantities of arachidic acid are stated to occur also amongst the solid fatty acids.

The proportion of stearic acid in the fat is as high as 39–40 p.c. Amongst the liquid fatty acids there seem to be present about 6 p.c. of acids less saturated than oleic acid, most likely linolic acid. From the iodine value of the cacao butter, viz. 34, the conclusion may therefore be drawn that it contains less than 30 p.c. of oleic acid. The unsaponifiable matter of cacao butter amounts to less than 1 p.c. Matthes and Rohdich found in the unsaponifiable matter a hydrocarbon (most likely identical with amyrilene), stigmasterol, and a phytosterol melting at 130°.

In the older literature, the statement frequently occurs, that cacao butter does not turn rancid. But it is a matter of common experience, as the writer has shown, that cacao butter, exposed to light and air at the ordinary temperature, becomes rancid in the course of time. Equally erroneous is the statement that rancid cacao butter is obtained from mouldy beans. Most shipments of cacao beans become mouldy in transit, but as the beans in the initial state of manufacture are roasted, the mould is destroyed, so that cacao butter prepared from these beans need not, of necessity, become rancid. With the growth of the consumption of chocolate and cacao, the trade in cacao beans has become of

very great importance. In 1907 the import of cacao beans into Europe and the United States of America amounted to about 220,000 tons. The consumption is still growing, and the imports may be expected to grow in proportion.

Cacao butter, being very high in price, even higher than cow butter, is frequently adulterated with, if not completely substituted by, 'chocolate fats.' The adulterants formerly employed, such as tallow and paraffin wax, are easily detected, and hence these adulterants have disappeared. The same holds good of coco-nut and palm-nut stearins, which, for some time, were largely used to adulterate cacao butter. Latterly, adulteration with cacao-shell butter has been practised and is still in vogue; for this purpose, the husks are ground and again expressed, or even extracted with volatile solvents. As the fat thus obtained yields, in analysis, practically the same characteristic numbers as genuine cacao butter itself, chemical analysis alone is unable to reveal adulteration with cacao-shell butter.

Cacao butter, being chiefly produced as a by-product in the manufacture of cocoa, is obtainable in large quantities: it is at present mainly used in the manufacture of cheaper chocolate. Smaller quantities are used in confectionery, in pharmacy for making suppositories and nitroglycerin tablets, and in the 'enfleurage' process of preparing delicate ethereal oils. J. L.

CACHALOT OIL. Oil obtained from the blubber of the cachalot. (For its properties and composition, *v.* Fendler, Chem. Zeit. 1905, 29, 555.)

CACODYLIC ACID and **CACODYLATES** *v.* ARSENIC, ORGANIC COMPOUNDS OF.

CADAVERINE *v.* PTOMAINES.

CADIE GUM *v.* GUMS.

CADINENE *v.* TERPINES.

CADMIUM. (*Kadmium*, Ger.) Sym. Cd. At. wt. 112·4.

Cadmium occurs in small quantities as sulphide in *Greenockite* at Bishopton, Renfrewshire, and in Pennsylvania and Bohemia. This is the only ore containing cadmium as the principal element. Cadmium occurs in small quantities in nearly all zinc ores, but the percentage is considerably lower than that usually stated. Jensch and Klieeisen have shown that the cadmium in zinc ores averages about 0·1 p.c., 0·5 p.c. being only reached in the richest samples, though occasional specimens are stated to have yielded considerably higher values. It occurs also in the silicate and carbonate of zinc at Freiberg, Derbyshire, and Cumberland, and in most commercial zinc.

Preparation.—In the reduction of zinc ores, the first portions of the distillate consist of a mixture of the metals zinc and cadmium and their oxides, but containing a higher percentage of cadmium (on account of its greater volatility) than the original ore, and by further similar treatment it is still further increased. When sufficiently rich, it is used for the extraction of the cadmium. At Silesia, the first portion of the distillate, which contains from 2 to 6 p.c. of cadmium, is mixed with about one-fourth of its weight of coal, and distilled at a dull red heat; the cadmium then distils with a little zinc, but the greater part of the latter metal remains behind. The cadmium is purified by fractional distillation until a product of 99·5 p.c. or more is obtained; it is then cast into small cylinders about ½ inch thick.

Various wet methods for the extraction of the cadmium from the concentrated flue dust, have been proposed and tried. Some of these are dependent on the precipitation of cadmium from acid solutions by means of zinc; others on the solubility of zinc in neutral ammonium carbonate. None of these wet methods, however, has been successful commercially (Schnabel and Louis, Metallurgy, 1907).

Electrolytic methods for the refining of cadmium, are employed, the cadmium being deposited on platinum electrodes and distilled *in vacuô*.

Properties.—Cadmium is a white metal with a tinge of blue, of strong lustre, and capable of taking a high polish. It produces a metallic streak on paper like lead, but less readily. Cadmium is compact in texture and of fibrous fracture, harder and more tenacious than tin, it may be drawn into thin wire or hammered into leaves, but when heated to 80° it becomes brittle, and may be powdered in a mortar. On account of its crystalline structure, it crackles, like tin, when bent.

By distillation in a current of hydrogen, cadmium may be produced in regular octahedra and other forms of the cubic system.

Cadmium melts at 321·7° (Holborn and Day), and boils at $[778+(h-760)/9]°$, where h is the barometric height in millimetres (Berthelot). Its vapour density at 1040° is 3·94 referred to air, or 56·3 referred to hydrogen. Hence it appears that the molecule of cadmium contains but one atom at that temperature, whilst further the values for the latent heat of vaporisation (calculated from the vapour pressure), indicate similar molecular states in liquid and gas (Traube). It is obtained in colloidal solution by electric sparking with a cadmium cathode in water.

According to Demarcay, it emits vapours when heated below the melting-point (Compt. rend. 95, 183). When heated in air, it burns readily, evolving brown fumes of the oxide. Cadmium dissolves in hydrochloric and sulphuric acids with evolution of hydrogen. It is readily attacked by nitric acid. It combines directly with chlorine, bromine, and iodine when placed in solutions of those elements. Cadmium gives a brilliant spectrum of red, green, and blue lines, and its use has been suggested as a convenient standard in refractometry (Lowry).

The salts of cadmium, as a rule, are but slightly dissociated in solution—this is especially so in the case of the iodide—and are hence liable to be incompletely precipitated by reagents.

Detection.—All compounds of cadmium, when heated on charcoal in the reducing flame, give a brown incrustation. Sulphuretted hydrogen produces a yellow precipitate in acid solutions, soluble in strong hydrochloric acid, insoluble in alkaline sulphides; it is thus distinguished from antimony and arsenic.

Estimation.—Cadmium may be precipitated as carbonate and weighed as oxide. Owing, however, to the reduction of the oxide and the great volatility of the metal, if filter papers are employed, the results are low, even when careful

precautions are taken. A Gooch crucible and asbestos filter should therefore be employed. Cadmium may also be estimated by precipitation from a neutral solution by excess of diammonium phosphate, and, after standing some time, collecting the precipitate on a weighed filter paper, dried at 105° (Page and Miller).

Electrolytic methods of estimation have also been found to be suitable and to yield accurate results. A cyanide solution with an E.M.F. of 3 to 3·5 volts and a current of 0·02 to 0·05 ampere, is a convenient arrangement (Rimbach).

To separate it from other metals not precipitable by sulphuretted hydrogen in acid solution, it is precipitated as sulphide by that gas, washed, dissolved in nitric acid, and precipitated with sodium carbonate.

Alloys of cadmium. The addition of cadmium to metals usually increases their fusibility without destroying their malleability.

The alloys with gold and copper are brittle; the others are usually ductile and malleable. With gold, a crystalline brittle silvery alloy, corresponding with AuCd, has been prepared, and the existence of a compound, Au_4Cd_3, is also indicated. Alloys, containing between 51 and 63 p.c. of cadmium, are very brittle. With platinum, a white crystalline compound appears to exist; and with copper compounds Cu_2Cd and Cu_2Cd_3, are indicated. The alloys rich in cadmium are steel-grey and soft, but become harder and more brittle with increase of copper up to 26·5 p.c., when the hardness again decreases and the yellow colour of copper appears. Researches by Rose on alloys of silver and cadmium indicate the existence of the compounds $AgCd_3$, Ag_2Cd_3, AgCd, Ag_3Cd_2, Ag_3Cd, and Ag_4Cd. Alloys containing over 80 p.c. silver are uniform and homogeneous, and well suited as material for trial plates for silver coinage and ware, for which the silver-copper alloy is not quite satisfactory. With sodium a compound, Cd_2Na, has been prepared, and compounds CdMg and $CdMg_4$ are indicated in the alloys with magnesium. The addition of ¼ p.c. cadmium to zinc increases the breaking strain, but more than ½ p.c. has the opposite effect. The amalgam, with mercury, was formerly used in dentistry, but its use has been discontinued, as it produces discolouration of the dentine. Multiple alloys, containing bismuth, frequently melt below 100°, and are used as fusible alloys; for these and other alloys containing bismuth and cadmium, *v. Alloys of bismuth*, art. BISMUTH.

Cadmium oxide CdO is prepared by heating the carbonate, in which case it is of a pale-brown colour; or by igniting the nitrate, when it is much darker and forms minute crystals. By heating cadmium in a current of oxygen, the oxide may be condensed in octahedral crystals; at low temperatures, some peroxide is also formed (Manchot). Cadmium oxide is infusible, insoluble in water, soluble in acids. It constitutes the brown deposit found in the condensers in the distillation of zinc.

Cadmium chloride $CdCl_2$ is prepared by evaporating the solution of the metal or oxide in hydrochloric acid. It melts below a red heat and sublimes at a higher temperature, condensing in micaceous plates.

Cadmium iodide CdI_2 is obtained by digesting 1 part of the metal with 2 parts of iodine in water and evaporating the solution. It crystallises in large transparent tablets, soluble in water and alcohol. It is used in medicine and, on account of its stability and solubility in alcohol, for iodising collodion plates in photography.

Cadmium sulphide. *Cadmium yellow; Jaune brillant.* This pigment may be produced by the addition of sulphuretted hydrogen or an alkaline sulphide to a solution of a cadmium salt. It may also be prepared by heating a mixture of cadmium oxide and excess of sulphur, but that produced by the former method is of a finer colour and has greater covering power.

It is an orange- or lemon-yellow powder, but may be obtained in prismatic crystals. When heated to redness, it becomes first brown, then carmine; it melts at a bright-red heat, and solidifies, on cooling, in laminæ of the original colour.

It is a very brilliant permanent colour. According to Jacquet, it is acted upon by light and by chlorine. It is much used as an oil and water colour, for colouring certain toilet soaps, for the production of a blue flame in pyrotechny, and in calico printing. The chief adulterants are compounds of zinc. According to Buchner (Chem. Zentr. 15, 329), two modifications exist: (1) the α-variety, precipitated by hydrogen sulphide in faintly acid solution; it is lemon-yellow, and possesses good covering power. When heated, it darkens temporarily to violet-red, but no permanent change occurs unless the temperature is high enough to produce oxidation. (2) The β-variety, produced in strongly acid solution; it resembles red lead, possesses good covering power, and is ordinarily quite permanent; if heated, it changes to the α-variety. Various shades are obtainable by mixture. The sulphide can also be obtained in colloidal solution.

Schmid (Dingl. poly. J. 241, 149) prepares a steam yellow for calico-printing as follows: 16 parts wheaten starch and 40 parts burnt starch are boiled in 1000 parts of water and mixed while hot with 350 parts of sodium thiosulphate. To the cooled solution, 350 parts of finely powdered cadmium nitrate are added with constant stirring until dissolved. This solution does not react in the cold, and may be applied to the fabric and steamed, the yellow sulphide being then precipitated.

Cadmium sulphate $CdSO_4,4H_2O$ is a very soluble salt prepared by dissolving the oxide or carbonate in sulphuric acid. It is used to some extent in medicine in place of zinc sulphate, especially on the Continent. It is also used in the construction of the Weston cell as a standard of E.M.F. The cell is usually made in the form of an H. One of the limbs contains mercury, covered by a paste of cadmium and mercurous sulphates. The other contains cadmium amalgam. Above both, to nearly the top of the limbs, which are closed by cork and wax, is a saturated solution, with crystals of cadmium sulphate. Through the glass of the lower limbs, platinum wires pass. The cell has an E.M.F. of 1·019 volts at 15°–18°, and has the advantage of a very low temperature coefficient.

Cadmium nitrate $Cd(NO_3)_2,4H_2O$ is prepared

by dissolving the oxide or carbonate in nitric acid. It crystallises in deliquescent fibrous needles, soluble in alcohol.

Cadmium salicylate is prepared from the acid and oxide or carbonate. It is readily soluble in alcohol, ether, or glycerol, and is used in medicine as an external antiseptic.

CÆSIUM. Symb. Cs. At. wt. 132·8. Cæsium was discovered in 1860 by Bunsen and Kirchhoff, in the Dürkheim water, being the first element detected by means of the spectroscope.

It is widely but sparsely distributed, usually in association with rubidium, as in the *lepidolite* from Hebron in Maine, U.S.A., which contains 0·4 p.c. cæsium oxide and 0·2 p.c. rubidium oxide; in *petalite*; in the mother liquors of the Nauheim salt spring, and in the ash of sea-weed, tobacco, tea, and other plants. Setterberg (Annalen, 210, 100) describes a method for the separation of cæsium and rubidium from the alums obtained as a by-product in the manufacture of lithia from lepidolite. Cæsium and rubidium chlorides are also obtained from carnallite by repeated fractional crystallisation. The cæsium is separated from the rubidium by the addition of antimony chloride, which precipitates only the cæsium in the form of the double salt $SbCl_3 \cdot 6CsCl$ (Feit and Kubierscky).

Cæsium occurs free from rubidium in the rare mineral *pollux*, from Elba, to the extent of 34 p.c. of cæsium oxide; to the extent of 1·71 parts of cæsium chloride per million in the water of the Wheal Clifford Mine (Yorke), and in the mineral waters of Frankhausen.

Cæsium may be prepared by electrolysis of a fused mixture of cæsium cyanide 4 parts and barium cyanide 1 part, using electrodes of aluminium (Setterberg). It is more readily obtained by heating the hydroxide with aluminium in a nickel retort, and condensing the metal in a glass receiver (Békétoff); or by heating the carbonate or hydrate with magnesium in a current of dry hydrogen (Graebe and Eckhardt). A more rapid method, yielding a better yield, is stated to be the reduction by calcium; 3 grams of this metal in small pieces with 12 grams of cæsium chloride are heated in a wide inverted Y-tube, the vertical limb being connected to a Sprengel pump. Reduction occurs at about 400°, and the cæsium volatilises and condenses in the vertical tube. It resembles rubidium and potassium in appearance, being silvery white, and soft at ordinary temperatures. It quickly oxidises in air, and rapidly decomposes water with ignition of the liberated hydrogen. Its sp.gr. at 15° is 1·88, its melting-point is 26°–27° (Setterberg).

Cæsium is the most electro-positive of all the elements. Its salts are stable, and have a strong tendency to form double salts. The salts are isomorphous with those of potassium and rubidium, and impart a more reddish tinge to the bunsen flame than salts of those metals. The hydroxide CsHO is a greyish-white highly deliquescent solid, melting below a red heat. The oxide Cs_2O is prepared by exposing the metal to insufficient oxygen and distilling off excess of cæsium; a peroxide CsO_2 is formed by heating to 300° in excess of oxygen (Rengade).

CAFFEINE *v.* VEGETO-ALKALOIDS.

CAFFEONE (*Caffeol*). A brown oil, heavier than water, and slightly soluble in boiling water. Constitutes the aromatic principle of coffee. May be obtained by distilling freshly roasted coffee with water, and agitating the distillate with ether, which dissolves out the oil. According to Lehmann and Wilhelm (Chem. Zentr. 1898, ii. 372), it has no physiological action on a healthy man (*v.* COFFEE).

CAFFETANNIC ACID *v.* TANNINS.

CAÏL-CEDRA. *Khaya senegalensis* (A. Juss.). A tree of the meliaceous order, growing on the banks of the Gambia and on the lowlands of the peninsula of Cape de Verde. Its bark is very bitter, and is much prized by the natives as a febrifuge, on which account it has been called the *cinchona of Senegal*. Its wood resembles American (Honduras, Cuba, Spanish) mahogany, is one of the so-called African mahoganies, and is used in making the finer kinds of furniture. The bark contains, amongst other substances, an extremely bitter, neutral resinous substance, called caïl-cedrin, to which its active properties appear to be due.

Caïl-cedrin is very sparingly soluble in water, but readily soluble in alcohol, ether, and chloroform. It is obtained by repeatedly exhausting the coarsely pulverised bark with boiling water; evaporating the filtered liquids over the water-bath to the consistence of a syrup; exhausting this extract with alcohol of 90 p.c.; precipitating the alcohol filtrate with basic lead acetate; filtering, distilling off the alcohol, and agitating the residue with chloroform, which dissolves nothing but the bitter principle. 1 kilogram of the bark yields about 8 milligrams of caïl-cedrin (Caventou, J. Pharm. [3] 16, 355; 33, 123).

CAÏNCETIN *v.* GLUCOSIDES.

CAÏNCIN *v.* GLUCOSIDES.

CAIRNGORM. A yellow or pale-brown transparent variety of quartz, largely used as an ornamental stone. A rich yellow tint is often produced artificially by the action of heat upon dull, smoky quartz. The mineral derives its name from Cairngorm (the Blue Mountain), one of the highest peaks of the Central Grampians. Most of the cairngorm of commerce is now obtained from Spain or from Brazil. Certain cairngorms bear a strong resemblance to yellow topaz, and are hence known to jewellers as 'Scotch topaz' or 'Spanish topaz.' The simplest way of distinguishing such false topaz from the true stone is to take its specific gravity (cairngorm 2·6, topaz 3·5). When determinations have to be made frequently, it is convenient to have Sonstadt's solution or other heavy liquid made up to a density of nearly 3. On dropping the stones into such a liquid, the true topaz sinks, while the cairngorm floats.

F. W. R.

CAJEPUT or **CAJUPUT OIL** *v.* OILS, ESSENTIAL.

CAJEPUTOL *v.* CAMPHORS.

'CAL' *v.* TUNGSTEN.

CALABAR BEAN *v.* ORDEAL BEAN.

CALABAR FAT *v.* PHYSOSTIGMINE.

CALABARINE *v.* VEGETO-ALKALOIDS.

CALAMINE. A term applied indifferently to both silicate and carbonate of zinc. In this country, the term is usually restricted to the carbonate, whilst the silicate is called *Smithsonite* or electric calamine (*v.* ZINC).

CALAMUS. The Indian variety of *Acorus*

calamus (Linn.); is used as a medicine in the Levant; the Turks candy it and employ it as a remedy against contagion. The volatile oil occasionally enters into the composition of aromatic vinegar. According to Thoms, *cicorin* $C_{36}H_{60}O_6$, in contact with ferments, splits up into sugar and oil of calamus

$$C_{36}H_{60}O_6 = C_6H_{12}O_6 + 3C_{10}H_{16}$$

(*cf.* von Soden and Rojahn, Chem. Zentr. 1901, i. 843; Thoms and Beckstroern, Ber. 1901, 34, 1021) (*v.* ACORUS CALAMUS).

CALCITE or **CALC-SPAR.** One of the dimorphous crystallised forms of calcium carbonate ($CaCO_3$). This rhombohedral form is less dense (sp.gr. 2·72) and less hard (H. 3) than the orthorhombic form aragonite (*q.v.*). It is also the more stable form: when aragonite is heated to low redness it passes into calcite, and paramorphs of calcite after aragonite are of frequent occurrence in nature. From an aqueous solution containing carbon dioxide, calcium carbonate crystallises as calcite at temperatures of 0°–18°, and as a mixture of calcite and aragonite at higher temperatures: the presence of various salts in the solution also favours the formation of aragonite. (For a summary of the literature on the crystallisation of calcium carbonate, *see* F. Vetter, Zeitsch. Kryst. 1910, xlviii. 45.) Calcite may be readily distinguished from aragonite by the possession of three perfect cleavages parallel to the faces of the primary rhombohedron, the angles between which are 74° 55′ and 105° 5′ (the plane angles on the rhomb-shaped faces are 78° and 102°). The mineral is readily scratched with a knife, and it effervesces briskly in contact with cold dilute acids.

With the exception of quartz, calcite is the commonest of minerals. It frequently occurs well crystallised and in a great variety of forms, the various forms of its crystals suggesting the trivial names 'dog-tooth-spar,' 'nail-head-spar,' 'paper-spar,' 'cannon-spar,' &c. As the essential constituent of the rocks limestone, marble, and chalk, it is of abundant occurrence. In these forms it finds extensive applications as building and ornamental stones, and in the manufacture of lime, mortar, and cement. The clear, transparent variety, known as Iceland-spar or doubly-refracting spar, is used in the construction of nicol prisms for optical polarising apparatus. Material suitable for this purpose is obtained almost exclusively from a quarry in basalt on the Reydar-fjördhr on the east coast of Iceland, but the supply is limited and variable.

L. J. S.

CALCIUM. Symbol Ca. At. wt. 40·0. Lime, the oxide of calcium, has been employed in the preparation of mortar from very early times. Interesting accounts of the process of lime-burning are given by Dioscorides and Pliny. It was not, however, until 1756 that the difference between burnt and unburnt lime was explained by Black.

Calcium is universally found as carbonate $CaCO_3$ in the forms of *calcspar*, *marble*, and *limestone*, often in whole mountain ranges or immense coral reefs. *Dolomite* or *bitter spar*, the double carbonate of calcium and magnesium, constitutes the geological formation termed magnesian limestone. Calcium sulphate as *anhydrite* $CaSO_4$ or *selenite* (*gypsum*) $CaSO_4 + 2H_2O$, is also very plentiful. The phosphate united with the chloride or fluoride also occurs widely distributed, often as minute inclosures in crystals of the primary rocks, as the mineral *apatite*, whilst calcium is an important base in the greater number of natural silicates. The solid matter carried away by rivers largely consists of the carbonate and sulphate of calcium, while sea-water contains, in addition to these, both phosphate and fluoride of calcium. The bones of animals consist largely of calcium phosphate, and the shells of molluscs of the carbonate. Calcium salts are never absent from plant tissues, concentrating mainly in the leaves.

Calcium also occurs in extra-terrestrial bodies, in the sun, meteorites, and many fixed stars.

Preparation of the metal.—Calcium was obtained as an impure metallic powder by Davy in 1808, by the electrolysis of the chloride, using mercury as negative electrode, and afterwards heating the amalgam thus formed until the mercury was volatilised. It was obtained as a metallic solid by Matthiessen in 1856 (Chem. Soc. Trans. 8, 28), by electrolysing a fused mixture of calcium and strontium chlorides in the proportion of two molecules to one with a little ammonium chloride, the whole being contained in a porcelain crucible. On passing the current, beads of metallic calcium separated at the negative pole and were ladled out. Moissan (Ann. Chim. Phys. [7] 18, 289) repeated the experiment, increasing the size of the apparatus, and obtained a metal possessing a yellowish colour.

Lies-Bodart and Gobin (Compt. rend. 47, 23) obtained calcium by heating the iodide with an equivalent of sodium in an iron crucible, the lid of which was screwed down. Moissan repeated the experiment several times, and states that the yield and purity vary greatly, the richest metal obtained containing from 83 p.c. to 93 p.c. calcium. The reaction proceeds best at a dull red heat, and is reversible if afterwards the temperature is raised to whiteness.

Frei obtained calcium in globules weighing 2·4 to 4 grams by the electrolysis of the chloride.

Another process consists in fusing 3 parts of calcium chloride with 4 parts of zinc and 1 part of sodium, thus forming an alloy of zinc and calcium, which, when heated in a gas-carbon crucible, decomposes, the zinc volatilising and a button of fused calcium remaining (Caron, Annalen, 115, 355).

Moissan obtained the alloy with facility, but was unable to separate the calcium from it.

Moissan (*l.c.*) points out that in all the above methods the difficulty is to free the calcium from the metal with which it has become associated in the preparation. He, however, finally succeeded in obtaining the pure metal by utilising the property, unknown before his researches, of molten sodium to dissolve calcium. For the preparation, he adopted a modification of the method of Lies-Bodart and Gobin. In an iron crucible of about 1 litre capacity he placed a mixture of 600 grams of coarsely crushed anhydrous calcium iodide, with 240 grams of sodium in pieces as large as nuts. The crucible was closed with a screw lid and maintained for 1 hour at a dull-red heat, then allowed to cool. The calcium, which is soluble in excess of sodium at a

red heat, separates at the point of solidification and becomes practically insoluble. The metallic portion of the melt is cut up into medium-sized fragments and gradually introduced into absolute alcohol. The sodium dissolves, leaving the calcium in brilliant white crystals, 98·9 p.c. to 99·2 p.c. pure.

Ruff and Plato have succeeded in obtaining the metal in relatively large quantities by the electrolysis of fused calcium chloride by keeping the temperature of the cathode above the melting-point of calcium (A. P. 806006). Borchers and Stockhem, by electrolysing fused anhydrous calcium salts, keeping the temperature of the cathode below the melting-point of calcium, obtained the metal in a spongy state (A. P. 808066). By using a vertical cathode, which only just touches the surface of the fused calcium salt, the metal is deposited on this surface, and by mechanically raising the cathode, an irregular shaped rod of calcium, resembling a cabbage stalk, is formed, which itself forms the cathode (E. P. 20655, cf. Johnson, J. Ind. Eng. Chem. 1910, 2, 466). The metal melts at 810°, and has a density of 1·548. It may be turned into cylinders having a brilliant lustre tarnishing in air. It may be drawn into wire of 0·5 mm. diameter. Its electric conductivity is 16, that of silver being 100.

Calcium is a white metal approaching silver in colour. It can be cut with a knife or broken with a blow, and the fracture is crystalline. It scratches lead, but not calcite. It is less malleable than sodium or potassium. The crystals are of tabular habit and belong to the rhombohedral system.

Gently heated in air, it burns with incandescence, or if heated in a current of air at a dull-red heat it leaves a spongy mass which decomposes water, producing ammonia and calcium hydroxide. Calcium, therefore, fixes both nitrogen and oxygen. Calcium inflames when heated in oxygen to 300°, and the heat is so great that the lime formed is both fused and partly volatilised. Fluorine gas violently attacks calcium at the ordinary temperature. Chlorine, bromine, and iodine have no action until heated to 400° or above. Water is attacked at the ordinary temperature with the liberation of hydrogen; the action is slow, owing to the formation of a crust of calcium hydroxide; the addition of sugar hastens the action. Fuming nitric acid attacks it only slowly if free from lime; the action is hastened on dilution. Fuming sulphuric acid is immediately reduced in the cold to sulphur and sulphur dioxide. Hydrochloric and acetic acids attack calcium violently, with the liberation of hydrogen. At a red heat, calcium reduces the fluorides and chlorides of potassium and sodium, setting free the alkali metals; under the same conditions, the iodides are not attacked.

Calcium, although soluble in molten sodium, from which it separates in the crystalline state on solidification of the solvent, is not notably soluble in potassium. With magnesium, it furnishes an alloy which decomposes cold water. With zinc and nickel, it forms brittle alloys. Tin, heated just above its point of fusion, combines with it with incandescence, forming a white crystalline alloy, containing 3·82 p.c. calcium.

Calcium hydride. CaH_2. Calcium does not unite with hydrogen at the ordinary temperatures. To prepare it, the metal cut into small pieces contained in several nickel boats, is placed in a glass tube sealed at one end. Hydrogen is fed in at a pressure of 4 to 5 cms. mercury, the tube being heated to redness; the temperature is kept sufficiently low to prevent union between the calcium and the nickel. So obtained, it is a fused white solid; sp.gr. 1·7. It may be heated to redness in air without change. Its characteristic reaction is the decomposition of water in the cold with the liberation of hydrogen.

Calcium oxide. Lime. CaO. Anhydrous calcium oxide (quicklime) is obtained by heating to redness any salt of calcium containing a volatile acid, as the carbonate and nitrate. Calcium carbonate, when heated in a closed vessel, may be fused without decomposition, but when raised to a red heat under ordinary pressure it gives off its carbon dioxide, and becomes converted into lime: $CaCO_3=CaO+CO_2$.

To obtain pure lime, Iceland spar or other forms of calcite, or the finest marble, may be employed, the ignition being performed in a crucible with perforated base so as to permit of the entrance of furnace gases, which carry away the carbon dioxide as fast as it is formed; otherwise the decomposition is incomplete, the carbonate undergoing no change in an atmosphere of carbon dioxide.

Lime is made by heating calcium carbonate to a temperature high enough to drive off the carbonic acid. The tension of dissociation of $CaCO_3$ is 27 mm. at 547° and 753 mm. at 812°; in practice, the temperature for burning lime is about 1000°. The raw material may be nearly pure calcium carbonate such as marble or chalk, or may contain so much clayey matter that the product is a cement of the Portland class rather than a lime. On this fact, choice of the mode of burning in part depends, because if the lime is needed to be pure it must be burnt out of contact with solid fuel, whereas if it is a cement rather than a lime, the addition of silicious matter from the ash of the fuel may be actually an advantage. The two chief uses of lime are for building and for chemical manufacture, and it is evident that for the former purpose, an impure limestone, burnt in contact with solid fuel, is to be preferred, whereas the purest obtainable limestone, heated out of contact with fuel, yields the best material for chemical use. In practice these principles are not always observed, partly from want of realisation of their validity and partly because it is sometimes economical to sacrifice the purity of the product rather than incur the expense in capital and fuel of kilns designed to burn limestone out of contact with solid fuel, but the knowledge of these is of value in deciding on the type of kiln to be adopted in any given case.

The simplest form of kiln is the flare kiln, shown in Fig. 1. The fuel (wood or peat) is burnt under an arch made of the material to be calcined, thus the lime produced is uncontaminated with ash. So crude a device is, of course, not economical of fuel, but its simplicity and cheapness, and the fact that it can produce excellent lime, cause it to be still used to a considerable extent.

Another simple form is the common running

kiln shown in Fig. 2. The limestone or chalk is loaded into the kiln with alternate layers of small coal or coke, and the product is from time to time drawn from an eye at the bottom

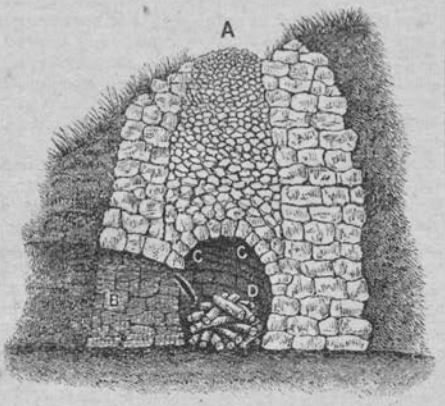


FIG. 1.

of the kiln, fresh layers of raw material and fuel being added through the charging hole at the top of the kiln. Lime made in a kiln of this class, of course, contains the whole of the ash of the fuel.

A more elaborate form of running kiln is the

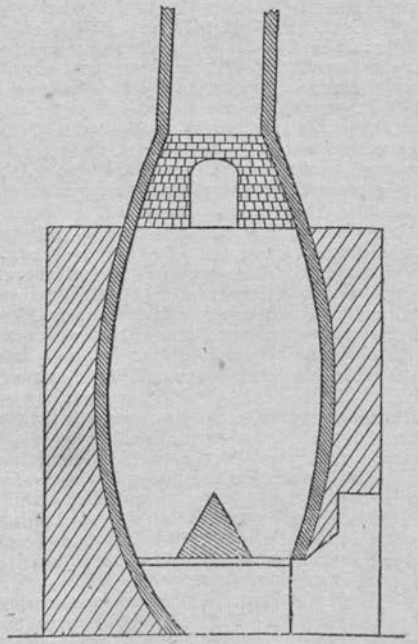


FIG. 2.

Copenhagen kiln, shown in Fig. 3. It is of the continuous-shaft type, the fuel and limestone being fed in at the top and the lime withdrawn at the bottom, but in addition a definite burning zone is established by feeding a portion of the fuel in at the side openings giving into the central part of the kiln. The heat can thus be controlled better than when all the fuel is distributed through the whole of the charge, with the result that consumption of fuel is decreased.

Another shaft kiln is the Ryan kiln, used in the Buxton district. Its construction is shown in Fig. 4. The fuel is fed in at the sides and the limestone at the top, so that the ash of the former is less inextricably mixed with the burnt lime. In consequence and because of the hardness and dense structure of Buxton limestone, a large part of the output is in lump practically uncontaminated with ash, so that the product

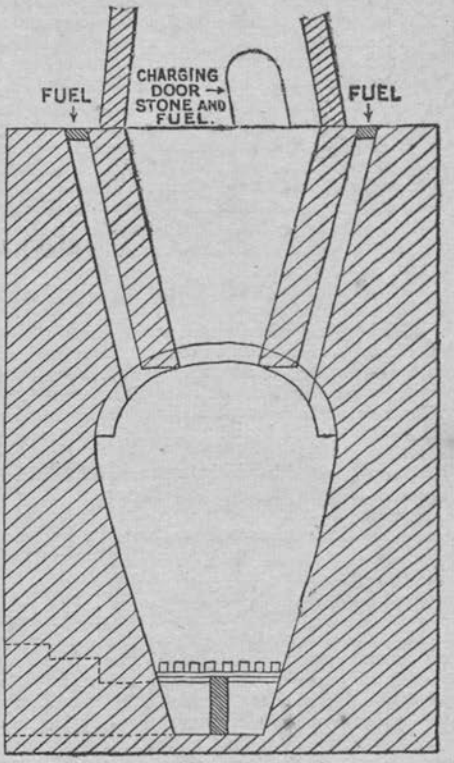


FIG. 3.—COPENHAGEN KILN.

can be picked and the lump of lime of high purity sold for chemical use, such as the manufacture of bleaching powder.

Lime can be burnt in a rotatory kiln, similar to those used for cement but worked at a lower temperature, but few such kilns are in use, the probable reason being that only small lime would be produced, and for many uses lump lime is preferred.

The Hoffmann kiln (Fig. 5) is used in places where labour is sufficiently cheap to allow of loading and unloading by hand being performed at a low cost; it has the advantage of being economical of fuel.

Passing from those kilns, like all the foregoing except the flare kiln, which allow at least some contact of the ash of the fuel with the lime, to gas-fired kilns in which contact is wholly avoided,

an intermediate type is found, illustrated by the Rumford kiln, shown in Fig. 6.

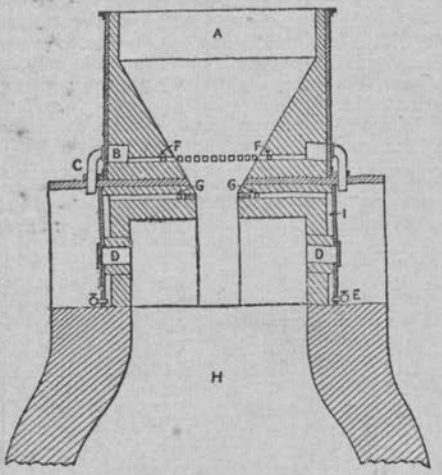


FIG. 4.

The fuel is burnt on the hearth of a furnace beneath a bridge up through which the gaseous products of combustion pass to the shaft of the kiln and over which descends the burnt lime to openings at the side, where it can be drawn.

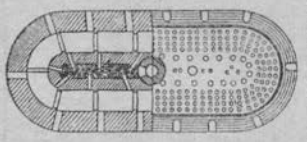


FIG. 5.

A gas-fired kiln proper is the Schmatolla kiln, shown in Fig. 7. Gas, from a producer at the side of the kiln, flows through ports in the walls of the kiln shaft, and there burns with a supply of secondary air, heated by passage through the hot lime which has descended below the level of the gas inlets. Kilns of this class have the advantages that they are continuous in operation, need but little labour, and allow the use of fuel too rich in ash to be suitable for burning in contact with the lime.

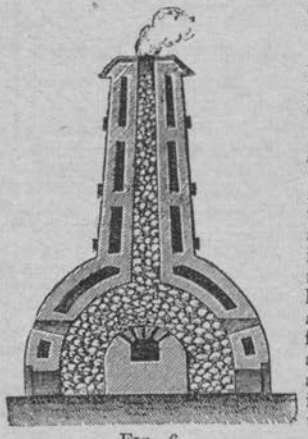


FIG. 6.

Qualities and uses of Lime.—Commercial lime ranges in composition from almost chemically pure calcium oxide to a material closely resembling Portland cement. The following analyses illustrate this:—

—	Buxton lime	Common building lime	Chaux de Teil	Blue Lias lime
Insoluble residue	0·71	13·20	0·62	2·39
Combined silica (SiO_2)		10·34	22·10	14·17
Alumina (Al_2O_3)	0·11			6·79
Ferric oxide (Fe_2O_3)		1·64	1·82	2·34
Lime (CaO)	98·72	51·10	66·72	63·43
Magnesia (MgO)	0·46	1·04	1·17	1·54
Sulphuric anhydride (SO_3)	—	0·21	0·49	1·63
Carbonic anhydride (CO_2)	—	8·00	0·64	3·64
Water (H_2O)	—	14·47	5·36	2·69
Alkalies and loss	—		1·08	1·38
	100·00	100·00	100·00	100·00

As mentioned above, the purest kinds are needed for chemical manufacture, and the less

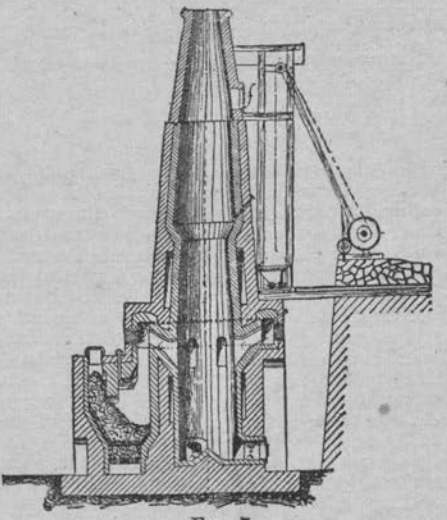


FIG. 7.

pure varieties which approach the nature of cement, are generally preferable for building. In the case of limes containing so much silica as does Chaux de Teil and so much silica and alumina as does Blue Lias lime, they may be regarded as hydraulic cements rather than limes proper. A rough trade distinction exists between 'fat' and 'poor' lime. The former is fairly pure and slakes rapidly and with a high rise of temperature; the latter, containing some combined silica and alumina, slakes slowly and relatively feebly. Both, when mixed with sand, form mortars, but fat lime sets only by drying and subsequent absorption of carbonic acid from the air, whereas the silicious constituents in poor lime will themselves set, to some small extent, in the manner of a cement. Pure lime, mixed with pure quartz sand, has no appreciable action on it at the ordinary temperature, but may act in slight degree on the more attackable silicious concomitants of common building sand; in any case, however, the action is trifling, and the setting of common mortar is practically unaffected by any such occurrence. In building, therefore, where an hydraulic cement is not

necessary, a moderately silicious lime, which will set lightly *per se*, is preferable to the fat lime commonly employed. In this country, lime is almost always slaked on the spot and at the time where it is to be used. Abroad, the lime is usually slaked long before it is used, and is thus allowed to become completely hydrated. The easiest plan is to make a paste of lime and water (lime putty), and keep it in a pit until it is needed. In like manner, slightly hydraulic lime is slaked with a limited quantity of water and allowed to remain in silos until the lime itself is completely hydrated, whilst the cementitious silicates remain unaffected and ready to act as cement when the lime is put to use.

When a dolomitic limestone is burnt, it yields a lime of which the following is an example :—

	Per cent.
Insoluble silicious matter	2·94
Alumina+ferric oxide (Al_2O_3+Fe_2O_3)	1·90
Lime (CaO)	46·72
Magnesia (MgO)	32·60
Sulphuric anhydride (SO_3)	0·92
Carbonic anhydride (CO_2)	3·27
Combined water and loss	11·65
	100·00

Lime of this kind needs much care in slaking, as the hydration of the magnesia takes place slowly and may occur after the mortar is in place, and by expansion cause destruction of the work.

Although lime will not act on sand at the ordinary temperature, yet, like other alkaline bodies it attacks it readily at a moderate temperature. The manufacture of sand-lime bricks is dependent on this fact. The bricks of sand, mixed with 5–10 p.c. of lime just hard enough to stick together, are exposed to steam at about 150° ; at that temperature the lime acts on the sand, producing calcium silicates, which are cementitious, and suffice to cement the sand grains together into a brick of ample strength for ordinary building purposes. In places where sand is abundant and clay suitable for brick making is scarce, the process is of considerable use.

Pure calcium oxide forms white porous amorphous masses of sp.gr. 2·3 to 3·08, highly infusible, melting only in the highest temperature of the oxyhydrogen blowpipe flame or in the electric arc. In the ordinary oxyhydrogen flame it emits an intense light, which is much used for lantern projection.

Calcium oxide has been obtained by Brügelmann in minute cubic crystals of sp.gr. 3·251 by heating the nitrate in a porcelain flask (Pogg. Ann. [2] 2, 466 ; and [2] 4, 277).

A crystalline mass, found upon the lining of a continuous limekiln at Champigny after 28 months' continuous work, was also shown to consist of small cubical crystals of pure lime, of sp.gr. 3·32 (Levallois and Meunier, Compt. rend. 90, 1566).

Amorphous lime takes up water with remarkable avidity, forming calcium hydroxide $Ca(OH)_2$, the combination being accompanied by a contraction in volume and evolution of heat. Owing to this property, it is used extensively in the laboratory and works as a drying agent. On exposure to air, the amorphous variety of lime rapidly absorbs water and carbon dioxide ; anhydrous lime, however, only absorbs the gas when heated to near 415°. Lime is readily soluble in dilute mineral acids. It also reacts with ethyl alcohol when heated in a sealed tube to 115° to 125°, giving a mixture of hydrate and ethylate of calcium.

Calcium hydroxide, or Hydrate of lime, $Ca(OH)_2$, is obtained by slaking fresh well-burnt quicklime with about a third of its weight of water. It forms a white amorphous powder of sp.gr. 2·078, sparingly soluble in water, and less so in hot than in cold water, as seen from the following table (Maben, Pharm. J. [3] 14, 505) :—

Temperature	Parts of water required to dissolve one part CaO	Temperature	Parts of water required to dissolve one part CaO
0°	759	55°	1104
5°	764	60°	1136
10°	770	65°	1208
15°	779	70°	1235
20°	791	75°	1313
25°	831	80°	1362
30°	862	85°	1388
35°	909	90°	1579
40°	932	95°	1650
45°	985	99°	1650
50°	1019		

According to Lamy (Compt. rend. 86, 333), the solubility varies slightly with the method of preparation of the hydroxide.

The solution known as lime water has an alkaline reaction, and absorbs the carbon dioxide of the atmosphere, forming a pellicle of calcium carbonate. Lime water of definite strength for pharmaceutical purposes, is best prepared by using freshly ignited lime. In preparing lime water from ordinary lime, the first solutions should invariably be rejected, as they will contain nearly all the soluble salts of the alkalis and the baryta and strontia present in the lime as impurities. Milk of lime is an emulsion of calcium hydroxide suspended in less water than is required for its complete solution. Calcium hydroxide is much more soluble in solution of sugar than in pure water, due to the formation of soluble saccharates (for solubilities, *v.* Weisberg, Bull. Soc. chim. 21, 773).

Calcium hydroxide is precipitated by caustic potash or soda from strong solutions of the chloride ; if a saturated solution of calcium chloride be employed, the whole becomes solid.

A solution evaporated over sulphuric acid in a vacuum deposits hexagonal prisms, according to Gay-Lussac. Crystals, however, which had separated on the surface of samples of hydraulic cement were found by Glinka to belong to the rhombic system in spite of their hexagonal appearance. A deposit of grey lamellæ, consisting of calcium hydroxide, was found by Luedecke in a Carré ice machine.

Calcium hydroxide is an energetic base combining with acids to form salts and displacing ammonia from its compounds.

At a red heat, calcium hydroxide is decomposed, water being driven off and oxide remaining.

Slaked lime is used extensively in the preparation of mortars and cements (*v.* CEMENTS), for softening hard waters, in the preparation of lyes and defecation of sugar, and for agricultural purposes.

Calcium dioxide CaO_2 was first prepared by Thenard by the action of excess of hydrogen peroxide upon lime water, when microscopic quadratic plates of the composition $CaO_2,8H_2O$, sparingly soluble in water and insoluble in alcohol, were precipitated. According to Conroy (Chem. Soc. Trans. 1873, 810), the peroxide is most conveniently prepared by adding lime water in considerable excess to an aqueous solution of sodium peroxide acidulated with nitric acid. It is also obtained as a finely divided white precipitate on adding a neutral or alkaline solution of sodium peroxide to a solution of a calcium salt. The crystals are isomorphous with those of hydrated barium peroxide. On exposure to air they effloresce, and when heated to 130° are converted into the anhydrous peroxide. On increasing the heat, half the oxygen is driven off, leaving a residue of pure lime.

Calcium chloride $CaCl_2$ is found in the water of nearly all springs and rivers, and is consequently a constituent of the saline matter dissolved in sea-water. This salt also forms the chief saline constituent of an exudation occurring on the face of the old red sandstone rocks at Guy's Cliff, in Warwickshire, occurring to the extent of 27·15 p.c. (Spiller, Chem. Soc. Trans. 1876, 1, 154). Calcium chloride likewise occurs, together with magnesium chloride and alkaline chlorides in the *tachydrite* and *carnallite* of the Stassfurt deposits, *tachydrite* containing 21 p.c. $CaCl_2$ and 36 p.c. $MgCl_2$, while *carnallite* contains 3 p.c. $CaCl_2$, and 31 p.c. $MgCl_2$.

Calcium chloride may be obtained by passing chlorine over the red-hot oxide, or by dissolving lime, chalk, or marble in hydrochloric acid and evaporating. If it is necessary to obtain the salt pure, chlorine water may be added to the solution in hydrochloric acid in order to oxidise any iron present, which may then be precipitated by the addition of milk of lime, and filtered off. The slightly alkaline filtrate is then acidified with hydrochloric acid and evaporated to the crystallising point.

Calcium chloride is obtained in large quantities as a by-product in many manufacturing processes, notably in the preparation of potassium chlorate and in the manufacture of sodium carbonate by the ammonia-soda process; it may be obtained in the pure state from these crude products by the method just indicated. Many attempts have been made to utilise this waste calcium chloride. Richardson (E. P. 10418) treats the purified crude solution with ammonium sulphate in the proportion required to convert all the chloride into sulphate; the calcium sulphate could then be filtered off, and ammonium chloride recovered by crystallisation. Pelouze (Compt. rend. 52, 1267) was the first to point out that calcium chloride mixed with sand to prevent fusion is almost completely decomposed when heated to redness and treated with steam, the chlorine being evolved as hydrochloric acid. The process was patented by Solvay, and the method applied to the waste calcium chloride liquors, but the condensed hydrochloric acid obtained is dilute and does not pay for the coal consumed in the operation. Lunge considers that so long as hydrochloric acid is so cheap, no possible method can be found to utilise the chlorine in the waste liquors at a profit.

Saturated solutions of calcium chloride deposit the hydrated salt in large hexagonal prisms terminated by pyramids, of the composition $CaCl_2,6H_2O$. The crystals melt at 29° in their water of crystallisation and deliquesce rapidly in the air, forming a viscous fluid, formerly termed *oleum calcis*. Heated below 200°, or in a vacuum over sulphuric acid, the crystals lose four molecules of water. The remaining two molecules can only be expelled above 200°. According to Weber (Ber. 15, 2316), the salt dried at 180°–200° is practically anhydrous, containing only 0·2 p.c. of water. Besides the two hydrates above described, Lescœur (Compt. rend. 92, 1158), from determinations of maximum tensions of solutions, shows the probable existence of two others $CaCl_2,4H_2O$ and $CaCl_2,H_2O$. The tetrahydrate, however, can only exist below 129°.

Anhydrous calcium chloride is a white porous mass, which fuses at a red heat or, according to Le Chatelier (Bull. Soc. chim. 47, 300), at 755°. On cooling, the salt solidifies to a translucent mass of crystals of sp.gr. 2·205. A slight decomposition into oxide and carbonate occurs when the fusion is performed in air. On this account, the porous chloride obtained by drying the crystals at 200° is better adapted for desiccating purposes, especially for the absorption of water in organic analysis. If the fused mass is exposed to the sun's rays, it becomes phosphorescent in the dark, and was formerly called *Homberg's phosphorus*, after the discoverer of the fact in 1693.

Anhydrous calcium chloride is highly deliquescent. 100 parts of the powder exposed to an atmosphere saturated with aqueous vapour absorb 124 parts of water in 96 days. According to Kremers (Pogg. Ann. 103, 57; 104, 133; J. 1858, 40), the following quantities of water are required to dissolve one part by weight of the anhydrous salt:—

At 10·2°	20°	40°	60°
1·58	1·35	0·83	0·72

In the following table, drawn up by the same author, are shown the specific gravities of solutions of varying strengths:—

Quantities in 100 parts water	Sp.gr. of solutions at 19·5° (water at 19·5°=1)
6·97	1·0545
12·58	1·0954
23·33	1·1681
36·33	1·2469
50·67	1·3234
62·90	1·3806

According to Engel (Bull. Soc. chim. 47, 318), 100 parts of water at 0° dissolve 60·3 parts $CaCl_2$, forming a solution of sp.gr. 1·367.

A solution of 50 parts anhydrous $CaCl_2$ in 100 parts water, boils at 112°, one containing 200 p.c. boils at 158°, and a 325 p.c. solution boils at 180°.

According to Lefebvre (Compt. rend. 70, 684), a supersaturated solution of calcium chloride is formed by dissolving 350–400 grams of the crystallised salt in 50 c.c. warm water or 200 grams of the anhydrous salt in 250 c.c. water; it may be shaken after cooling without crystallisation, but solidifies on contact with a crystal of the salt. If cooled to 5·8°, this solution begins to crystallise, the temperature rising to 28°–29°. A solution containing 55 p.c. $CaCl_2$ deposits at about 15°

large plates of the tetrahydrate $CaCl_2,4H_2O$, which do not induce the crystallisation of the supernatant liquor. This solution, in passing from liquid to solid state, undergoes at 70° a contraction 0·0832 of its volume.

The crystallised chloride $CaCl_2,6H_2O$ also deliquesces rapidly, and dissolves in half its weight of water at 0°, in one-fourth its weight at 16°, and in all proportions of hot water. In dissolving it absorbs heat, while the anhydrous chloride dissolves with evolution of heat. A mixture of 1·44 parts crystallised chloride with 1 part of snow produces a cold of −54·9°, more than sufficient to freeze mercury.

Both the anhydrous and hydrated chloride dissolve readily in alcohol, 10 parts at 80° dissolving 6 parts anhydrous $CaCl_2$; on evaporation in a vacuum at winter temperature, rectangular plates of $2CaCl_2,7C_2H_6O$ are deposited.

Anhydrous calcium chloride absorbs ammonia gas, forming the compound $CaCl_2,8NH_3$ as a white powder, which, on exposure to air, solution in water, or on heating, is decomposed. Thrown into chlorine gas, the compound takes fire.

Calcium oxychloride. When calcium chloride solution is boiled with slaked lime, and the liquid filtered, white needle-shaped crystals of calcium oxychloride separate out on cooling of the composition $ClCa·O·Ca(OH),7H_2O$ or $3CaO·CaCl_2,15H_2O$ (Grimshaw, Chem. News, 30, 280). The salt is stable out of contact with air, loses part of its water of crystallisation over sulphuric acid or caustic lime, and absorbs carbon dioxide from the atmosphere. It is decomposed by water or alcohol.

According to André (Compt. rend. 92, 1452), the composition of the salt is

$$CaCl_2·3CaO,16H_2O$$

and, on drying in a vacuum, it becomes converted into $CaCl_2·3CaO,3H_2O$.

When calcium chloride is fused at a bright-red heat in a current of moist air, it is gradually converted to an oxychloride of the composition $CaCl_2·CaO$, and eventually to oxide (Gorgeu, Compt. rend. 99, 256).

Calcium hypochlorite *v.* BLEACHING POWDER.

Calcium chlorate $Ca(ClO_3)_2$ is produced when chlorine is passed into hot milk of lime, but is difficult to separate from the chloride simultaneously formed. This is the first step in the manufacture of potassium chlorate, and the reaction is supposed to be as follows:—

$$6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O.$$

According to Lunge (J. Soc. Chem. Ind. 1885, 722), the reaction really takes place in several stages, calcium hypochlorite and hypochlorous acid being first formed and mutually reacting with production of calcium chlorate:

(1) $Ca(OCl)_2+4Cl+2H_2O=CaCl_2+4HClO.$
(2) $2Ca(OCl)_2+4HClO=CaCl_2+Ca(ClO_3)_2+4Cl+2H_2O.$

The free chlorine serves only as carrier of the oxygen of two molecules calcium hypochlorite to a third molecule of the hypochlorite which is oxidised to chlorate. Lunge's experiments show that the best mode of converting hypochlorite into chlorate is to raise the temperature of the solution, slight excess chlorine being at the same time present. The heat produced by the reaction on the large scale is sufficient.

Calcium chlorate can best be prepared by the electrolysis of a 10 p.c. solution of calcium chloride. The density of the current should be 10 amperes per square decimetre at the anode and double at the cathode; temperature 50° (Zeitsch. Elektrochem 4, 464).

Pure calcium chlorate is prepared by precipitating potassium chlorate with calcium silicofluoride. It crystallises in deliquescent rhomboidal plates, very soluble in water and alcohol; the crystals contain 16·5 p.c. water, melt when warmed, and decompose on further heating.

Calcium perchlorate $Ca(ClO_4)_2$ may be obtained by saturating perchloric acid with caustic lime. It is extremely deliquescent and crystallises in prisms soluble in alcohol.

Calcium bromide $CaBr_2$ is formed by burning calcium in bromine vapour, or by dissolving lime or calcium carbonate in hydrobromic acid and evaporating. The silky needles thus obtained are hydrated, but may be converted to the anhydrous salt by heating. Calcium bromide much resembles the chloride in properties, being deliquescent, and very soluble in alcohol.

Calcium iodide CaI_2 may also be prepared by combustion of calcium in iodine vapour, or by solution of lime or the carbonate in hydriodic acid, evaporating and fusing the residue in a closed vessel. Heated in contact with air, it fuses below a red heat, and is decomposed with liberation of iodine vapours and formation of lime.

Liebig (Annalen, 121, 222) recommends decomposition of CaI_2 by K_2SO_4 for preparation of iodide of potassium. To prepare the calcium iodide, 1 oz. of amorphous phosphorus is drenched with 30 oz. hot water, and finely pulverised iodine gradually added with constant stirring as long as it dissolves without colour (quantity thus dissolved being 13½ oz.). The colourless liquid is then decanted from the slight deposit, and made slightly alkaline with milk of lime (8 oz. lime being required); the solution is afterwards strained, and residue of phosphate, phosphite, and hydrate of calcium washed. The solution then contains the calcium iodide, which may, if necessary, be obtained by evaporation in the form of hydrate in deliquescent needles.

A double iodide of calcium and silver of the composition $CaI_2·2AgI,6H_2O$ has been prepared by Simpson (Proc. Roy. Soc. 27, 120) by saturating a hot concentrated solution of CaI_2 with moist silver iodide. It crystallises on cooling in long white needles, decomposed by water.

Calcium iodate $Ca(IO_3)_2$ is obtained by crystallising mixed solutions of potassium iodate and calcium chloride. The hydrated salt forms four-sided prisms which effloresce in the air, and become anhydrous when heated to 200°. From a solution acidulated with nitric acid, it separates in trimetric crystals. The crystals are soluble in 454 parts water at 18°, and in 102 parts of boiling water, but are insoluble in alcohol. The anhydrous salt, gently heated in a porcelain retort, evolves 14·78 p.c. of oxygen, and 54·07 of iodine, leaving 31·14 p.c. of a residue rich in pentabasic periodate of calcium. Heated more strongly, it evolves more oxygen and iodine, and leaves 20·35 p.c. of a mixture of pentabasic periodate and free lime. Calcium iodate detonates violently when heated on charcoal.

Sonstadt proposes (E. P. 6304, 1884) to use calcium iodate as an antiseptic.

Periodates of calcium. When the sodium

salt NaH_4IO_6 is decomposed by calcium nitrate, a crystalline white precipitate of dicalcium periodate CaH_3IO_6 or $2CaO{\cdot}3H_2O{\cdot}I_2O_7$ is obtained. When this salt is heated, water, oxygen, and iodine are given off and pentacalcium periodate $Ca_5I_2O_{12}$ remains (Langlois).

Calcium fluoride CaF_2 is found widely distributed in nature and is known as *fluor-spar*. It is the only common mineral in which fluorine forms one of the principal constituents. It occurs both massive and in beautiful crystals, generally cubes or forms in combination with the cube. It is a common vein mineral, occurring usually in association with metallic ores, barytes, calcite, &c. It presents a variety of colours, sometimes shading into one another as in the beautiful 'Blue John' of Derbyshire. Free fluorine has been shown to exist in a dark violet fluor spar from Quincié, Dept. du Rhône. It is also a constituent in small quantities of many plant ashes, of bones, and of the enamel of teeth. When calcium fluoride, obtained by precipitating any soluble calcium salt with fluoride of sodium or potassium, is heated with water slightly acidified with hydrochloric acid, the precipitate is found to consist of microscopic octahedrons.

Calcium fluoride is soluble in about 2000 parts of water at 15°, and is slightly more soluble in water containing carbon dioxide. It dissolves in hydrofluoric acid and in strong hydrochloric acid, and is precipitated in the gelatinous form by ammonia. It is fusible at 902°, and is used as a flux in many metallurgical operations, especially in the reduction of aluminium. It is decomposed at a high temperature by water vapour into lime and hydrofluoric acid. Fusion with alkaline carbonates or hydroxides yields carbonate or oxide of calcium and alkaline fluorides. Strong sulphuric acid, on gently warming, decomposes it, forming calcium sulphate and liberating hydrofluoric acid. At a red heat it is also decomposed by chlorine. After being heated fluor spar phosphoresces in the dark. There is a considerable industry carried on in fluor-spar districts in the carving of ornamental vases and other articles, the brilliantly coloured varieties being especially in demand.

Calcium carbide CaC_2. Wöhler (Ann. Chim. Phys. 125, 120) showed that by the action of carbon on a molten alloy of zinc and calcium, a black mass is obtained, which on contact with cold water liberates various gases. Winkler indicated the reduction of the alkaline earths by magnesium (Ber. 22, 120). Maquenne, in 1892, prepared calcium carbide as an impure amorphous black powder, and Travers obtained it by heating together calcium chloride, sodium, and carbon. It was not, however, until the advent of the electric furnace that it became possible to manufacture a pure carbide suitable for the preparation of acetylene. Moissan (Compt. rend. 138, 243) used a mixture of lime 120 grams, sugar carbon 70 grams, which was heated in the crucible of an electric furnace for 20 minutes with a current of 350 amperes and 70 volts. At the temperature of liquefaction of the lime, this reaction occurs: $CaO+3C=CaC_2+CO$. Pure calcium carbide is crystalline, colourless, and transparent, but the commercial variety, discoloured by iron, is usually brownish-red. Its characteristic reaction is the decomposition of water in the cold, with the liberation of acetylene and the formation of calcium hydroxide.

In the modern industrial method, as for instance the Alby United Carbide Factories, Ltd., Odda, Norway, lime and anthracite are employed and the electricity is generated by water power. Producer-gas fired kilns are used for burning the lime. There are 12 electric furnaces of 1400 kilowatts capacity in use, and the current supplied is 28,000 amperes at 50 volts. The charging is practically constant and the carbide is tapped at intervals of about 45 minutes. The temperature used is about 3000°.

One of the most interesting developments of the manufacture is the production of 'nitrolin,' calcium cyanamide $Ca(CN)_2$, from calcium carbide for manurial purposes. The nitrogen required is obtained from the air by the Linde Company's plant, which produces both nitrogen and oxygen. The union of powdered calcium and nitrogen takes place with the evolution of heat, hence the temperature has to be maintained between 800°–1000°, as at higher temperatures the calcium cyanamide decomposes. The absorption occupies 30 to 40 hours, and the product is a cokelike material which is ground to powder before being placed on the market (*v.* NITROGEN, UTILISATION OF ATMOSPHERIC).

Calcium carbonate $CaCO_3$ occurs naturally in the forms of limestone, chalk, marble, and calcite; it also constitutes the principal ingredient in egg-shells, mollusc-shells, and coral. It is formed when the oxide or hydroxide is exposed to moist air containing carbon dioxide, but is not produced by the action of dry carbon dioxide on dry lime. It may be obtained in the pure state by dissolving chalk or marble or calcined oyster-shells in hydrochloric acid, precipitating the alumina, oxide of iron, and earthy phosphates by ammonia or milk of lime, filtering, then precipitating the calcium by ammonium carbonate, washing and drying.

Calcium carbonate is dimorphous, crystallising in the hexagonal system as calcite (*q.v.*) and in the rhombic system as aragonite (*q.v.*).

A litre of water dissolves about 18 milligrams of calcium carbonate. The solution has a slight alkaline reaction. Water containing carbonic acid dissolves it much more readily, forming the acid carbonate $CaH_2(CO_3)_2$, which is known only in solution. Solubility at higher pressures in water containing carbonic acid follows the law of Schloesing pretty closely (Engel, Compt. rend. 101, 949). The solubility increases under an increase of pressure only up to 3 grams per litre according to Caro. One litre of water saturated with carbon dioxide dissolves 0·7 gram of the carbonate at 0°, but 0·88 gram at 10°. This acid carbonate plays a most important part in nature, for whenever water containing carbonic acid comes in contact with carbonate or silicates of calcium, the calcium is gradually converted into this soluble form, and is therefore found in almost all natural waters. Hence also the deposits in kettles and boilers; the formation of which may be prevented by the addition of ammonium chloride to the water.

Calcium carbonate, when heated to full redness in open vessels, is decomposed into lime and carbon dioxide. The decomposition commences at a low red heat, and in a current

of air, or better steam, the temperature of dissociation is lower still. The tension of dissociation becomes equal to the pressure of the atmosphere, according to Le Chatelier (Compt. rend. 102, 1243), at about 812°. If heated rapidly, the stationary temperature of dissociation is 925°. At 547° the tension of dissociation is 27 mm.; at 610°, 46 mm.; at 625°, 56 mm.; at 740°, 245 mm.; at 810°, 678 mm.; and at 865°, 1333 mm. If the carbonate be ignited in a closed vessel, it fuses, resolidifying to a mass of marble-like calcite. According to Becker (Jahrb. Min. 1886, 1, Ref. 403), any form of $CaCO_3$, even at a low pressure, is changed on heating in a closed space with exclusion of air into the rhombohedral form without fusion. If small quantities of the precipitated carbonate are thrown into a fused mixture of sodium and potassium chlorides in equivalent proportions, no carbon dioxide is evolved, but the carbonate becomes crystalline calcite, usually in aggregations of crystals like snow crystals (Bourgeois, Bull. Soc. chim. [2] 37, 447).

Pentahydrated calcium carbonate

$CaCO_3,5H_2O$.

The evaporation of natural solutions of the acid carbonate generally results in the deposition of the ordinary carbonate, forming the stalactites and stalagmites of caverns, travertine, and other forms of deposit; but sometimes the solution yields six-sided rhombic prisms of the composition $CaCO_3,5H_2O$. These crystals are often found in pumps and pipes leading from wells, also adhering to the confervæ in ponds. They keep unaltered under water at 20°, but at slightly higher temperatures lose their transparency and water of crystallisation In air they crumble to powder through loss of water (Pfeiffer, Arch. Pharm. [2] 15, 212). This salt, according to Pelouze (Ann. Chim. Phys. [2] 48, 301), is obtained in small acute rhombohedra, sp.gr. 1·783, by boiling lime in a concentrated solution of sugar, starch, or gum, and leaving the solution for some months in a cold place. Becquerel, by exposing a solution of lime in sugar water to a voltaic battery of 12 cells, obtained crystals of the same composition, but in form of rhombic prisms.

Basic carbonates of lime. Calcium oxide commences to absorb carbon dioxide at a temperature of 415°, forming a basic carbonate of the composition $2CaO·CO_2$ (Birnbaum and Mahu, Ber. 12, 1547).

Raoult (Compt. rend. 92, 1457) shows that when freshly burnt lime is heated in a current of carbon dioxide, it glows strongly, forming $2CaO·CO_2$, which does not disintegrate in moist air, and does not take up water from steam at 200°. When finely powdered and treated with a little water, it hardens like hydraulic cement. The hydrated product has the composition $CaCO_3·Ca(OH)_2$. On heating to dull redness, it loses water and is converted into a mixture of $CaCO_3$ and CaO.

When burnt lime is heated in contact with carbon dioxide for several days, the basic salt $2CaCO_3·CaO$ is obtained, which still absorbs CO_2, forming a third salt $3CaCO_3·CaO$. The carbon dioxide continues to be absorbed, however, and appears eventually to form the normal carbonate.

Calcium nitride Ca_3N_2 is best obtained by passing dry nitrogen over metallic calcium contained in a nickel boat and tube heated to bright redness. Two to three hours are required, and the resulting material is fritted and possesses a brownish-red colour. Its fusion point is about 1200°; sp.gr. 2·63 at 17°. When thrown into water it produces a lively effervescence, yielding ammonia and calcium hydroxide

$$Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$$

(Moissan, Ann. Chim. Phys. [7] 18, 289).

Calcium ammonium $Ca(NH_3)_4$ is formed when a current of dry ammonia gas is passed over metallic calcium, maintained at a temperature of 15° to 20°. It possesses a brownish-red colour, and takes fire when exposed to air.

Calcium amide $Ca(NH_2)_2$. Calcium ammonium slowly decomposes, forming transparent crystals of calcium amide, hydrogen and ammonia being evolved.

Calcium nitrite $Ca(NO_2)_2,H_2O$ is prepared by decomposing a boiling solution of silver nitrite with lime water, treating the filtrate with sulphuretted hydrogen and carbonic acid to remove excess of silver and calcium, and evaporating at a gentle heat. It crystallises in deliquescent prisms insoluble in alcohol.

Calcium nitrate $Ca(NO_3)_2,4H_2O$ occurs as a silky efflorescence in limestone caverns, especially those of Kentucky, also on the walls of places where there is much organic refuse. It is found in many well waters, being derived from the soil. It is extremely deliquescent and soluble, and causes rapid disintegration of mortar, and hence is called 'saltpetre rot.' It may be prepared by dissolving the carbonate in nitric acid, the solution depositing on slow evaporation monoclinic six-sided prisms terminated by acute pyramids of the above composition. On evaporating the solution to dryness, the anhydrous salt of sp.gr. 2·472 is obtained, possessing a warm bitter taste and readily soluble in water and alcohol. On heating more strongly, it becomes phosphorescent, as noticed by Baldwin in 1674, and hence is termed *Baldwin's phosphorus*. At a higher temperature, oxygen and nitric peroxide are evolved, and with combustible bodies detonation occurs. It is extensively prepared on the Continent for the manufacture of nitre by mixing vegetable and animal refuse with chalk, marl, cinders, &c., moistening from time to time with liquid stable manure, and exposing to the air for two or three years, when the mass is lixiviated and the crude nitrate of calcium decomposed by carbonate, sulphate, or chloride of potassium.

Calcium phosphide. Moissan (Compt. rend. 128, 787) prepared calcium phosphide from pure crystallised calcium and red phosphorus. The two bodies were placed apart in a tube which was exhausted and the phosphorus was gently heated. The vapours evolved combined with the calcium with incandescence. He also obtained it by reduction of pure calcium phosphate with carbon in an electric furnace, using 310 parts and 96 parts respectively of the ingredients and a current of 950 amperes and 45 volts. So obtained, it is a brownish-red body, crystalline when prepared in the electric furnace. Its characteristic reaction is the decomposition of water in the cold with the production of calcium hydroxide and hydrogen phosphide. Prepared

by either of the above methods, it has the composition Ca_3P_2.

Thenard (Ann. Chim. Phys. [3] 14, 12) obtained calcium phosphide mixed with phosphate by passing the vapour of phosphorus over red-hot lime. The substance may be prepared on a larger scale by filling a crucible with a hole in its base with pellets of lime, and placing it upon the grate of a furnace. A flask containing phosphorus is placed below the grating with its neck passing into the hole of the crucible. When the lime has been heated to redness, the phosphorus is gradually heated so that its vapour passes through the lime. The brown mass is stated by Gmelin (Handb. 3, 188) to be a mixture of monocalcium phosphide and tricalcium phosphate.

When thrown into water, the product is instantly decomposed with evolution of spontaneously inflammable phosphoretted hydrogens.

Owing to this property, calcium phosphide is utilised for the production of signal fires at sea. The manufacture is carried on in an arrangement similar to the above, the crucibles being larger and divided by a false perforated bottom into two compartments, in the upper of which the pieces of lime are raised to a red heat, the phosphorus placed in the lower compartment being afterwards volatilised by the heat radiated from above. In about 6 hours, a charge, yielding 20 lbs. of product, is finished. The brown stony mass is immediately worked up into the 'lights.', These consist of cylindrical tinned-iron boxes, the lower half of which is filled with about 16 oz. of the fragments of phosphide. Two small circular portions of the upper and under surfaces of metal are formed of soft lead, so that they may be pierced by a knife just before being thrown overboard. The tins are supported by a wooden float when in use. The water enters below and the gas issues from the upper outlet, burning with a flame 9 to 18 inches high, lasting about half an hour. Larger but similar 'lights' are prepared to be placed in a bucket of water on deck. In the British Navy torpedo practice, a peculiar form of the phosphide is also used.

Calcium phosphite $CaHPO_3,H_2O$ separates as a crystalline crust from a solution of the ammonium salt mixed with calcium chloride. It is sparingly soluble in cold water, and the solution decomposes when heated, depositing a basic salt, an acid salt remaining dissolved. It gives off its water at 100°. It is a white crystalline powder, which, on heating, evolves spontaneously inflammable phosphoretted hydrogen, accompanied by slight detonations. At a certain temperature, it becomes incandescent, and leaves a residue of calcium phosphate.

An acid phosphite $CaH_4(PO_3)_2,H_2O$ is obtained as a crystalline crust by acting upon marble with aqueous phosphorous acid as long as carbon dioxide escapes. The crust consists of needle-shaped crystals soluble in water, and losing their water at 100°.

Calcium hypophosphite $Ca(PO_2H_2)_2$ or $CaH_4(PO_2)_2$ is used medicinally, and is prepared by boiling phosphorus with milk of lime

$3Ca(OH)_2+2P_4+6H_2O=2PH_3+3CaH_4(PO_2)_2$.

On evaporation the hypophosphite is obtained in monoclinic flexible prisms insoluble in alcohol. When heated it evolves phosphoretted hydrogen and water, leaving calcium pyrophosphate.

Calcium orthophosphate $Ca_3(PO_4)_2$ occurs pure in the mineral *osteolite*, and as

$Ca_3(PO_4)_2,2H_2O$

in *ornithite*. Combined with calcium fluoride or chloride, it occurs in nature as *apatite*

$3Ca_3(PO_4)_2+CaF_2$

in which form it is found in large crystals in the metamorphic limestones at Burgess, Ontario, Canada. The massive variety, phosphorite, is mined on a large scale at Odegarden, Norway In certain apatites, the CaF_2 is more or less replaced by $CaCl_2$.

Calcium phosphate also forms a principal constituent of the coprolites frequently found in extensive beds in the stratified rocks. This material forms the principal source of the rock phosphate of commerce. It is the chief inorganic material of bones, forming about 80 p.c. of burnt bones.

It is obtained in the amorphous state by precipitating an ammoniacal solution of calcium chloride with excess of hydrogen disodium phosphate. The precipitate is gelatinous, but dries up to a white earthy powder, nearly insoluble in water, but is decomposed by long boiling into an insoluble basic salt of the composition

$Ca_3(PO_4)_2{\cdot}Ca_2(PO_4)OH$

and a soluble acid salt. This reaction also occurs slowly in the cold. Calcium phosphate is also soluble in water containing carbonic acid (1 part in 1789 parts of water saturated with carbon dioxide), ammonium salts, sodium nitrate, sodium chloride, and other salts. Its absorption by the roots of plants is therefore promoted by the agency of saline solutions.

Freshly precipitated calcium phosphate combines with sulphur dioxide, becoming soluble in water. On heating the solution, some of the gas is liberated and a crystalline precipitate, having the composition $Ca_3SO_2P_2O_8,2H_2O$, is formed, a compound which is very stable (Ber. 15, 1441).

Calcium orthophosphate may be obtained in the crystalline form by heating dicalcium pyrophosphate with water, whereby it is resolved into phosphoric acid and tricalcium phosphate, which separates in rectangular plates

$3Ca_2P_2O_7+3H_2O=2Ca_3(PO_4)_2+2H_3PO_4$.

Tricalcium phosphate is not decomposed by ignition.

Dicalcium orthophosphate $Ca_2H_2(PO_4)_2$. An aqueous solution of phosphoric acid acts on precipitated chalk, forming small needle-shaped crystals of dicalcium phosphate. Dried at 100°, the salt contains $5H_2O$, which it does not lose below 115°. It is soluble in ammonium citrate, Boiled with water, it is partially decomposed into tricalcium phosphate.

On mixing boiling solutions of sodium phosphate, calcium chloride, and acetic acid,

$Ca_2H_2(PO_4)_2,H_2O$

is formed; if the solutions are mixed in the cold, $Ca_2H_2(PO_4)_2,5H_2O$ is formed (Millot, Bull. Soc. chim. [2] 33, 194). The salt is also formed (Joly and Sorrel, Compt. rend. 118, 741) when saturated solutions are mixed in the cold if hydrochloric acid is added.

When a solution of calcium chloride is mixed with one of ordinary sodium phosphate, a white crystalline precipitate of $Ca_2H_2(PO_4)_2,4H_2O$ is

thrown down. It is this salt which is occasionally deposited from wine in stellar aggregates. According to Becquerel and Berzelius, a trihydrate may also be obtained. These different results as regards water of crystallisation are probably owing to the fact that the precipitates vary in amount of water and solubility in acids according to the conditions of their precipitation.

Monocalcium phosphate $CaH_4(PO_4)_2$ is obtained in rhombic tables by dissolving either of the former phosphates in phosphoric acid and allowing the solution to spontaneously evaporate. It has a strong acid reaction, and deliquesces in air, dissolving readily in water. A small quantity of water decomposes it, forming insoluble dicalcium phosphate and free phosphoric acid. If cold, the hydrate $Ca_2H_2(PO_4)_2,4H_2O$ is formed; if hot, the same salt, free from water, is precipitated.

Monocalcium phosphate fuses on heating, giving up its water, and when heated to 200° it parts with the elements of water, leaving a mixture of calcium pyrophosphate and metaphosphoric acid

$$2CaH_4(PO_4)_2 = Ca_2P_2O_7 + 2HPO_3 + 3H_2O.$$

When the mixture is heated to a still higher temperature, pure calcium metaphosphate remains.

Superphosphate of lime is a mixture of monocalcium phosphate and calcium sulphate, which is manufactured as a manure. It is prepared by acting on bone-ash, rock phosphate, phosphorites, or other mineral phosphates with two-thirds their weight of sulphuric acid:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

Besides its use as a manure for root-crops, it is used in the manufacture of phosphorus (*v.* FERTILISERS).

Calcium pyrophosphate $Ca_2P_2O_7$ is prepared by action of aqueous pyrophosphoric acid upon lime water, or sodium pyrophosphate upon calcium chloride. If the precipitate thus obtained is dissolved in sulphurous acid and the solution heated, the salt separates as a crystalline crust. The crystals contain four molecules of water.

Calcium metaphosphates. The monosalt $Ca(PO_3)_2$ is obtained by dissolving calcium carbonate in orthophosphoric acid, evaporating, and heating the residue to 316°. It is an insoluble white powder.

The dimetaphosphate $Ca_2(PO_3)_4,4H_2O$ is obtained pure in the crystalline form by precipitating the corresponding alkali salt with excess of calcium chloride. It is insoluble in water, but is decomposed by strong sulphuric acid. A double dimetaphosphate of calcium and ammonium $Ca(NH_4)_2(PO_3)_4,2H_2O$ is obtained in spicular crystals by mixing a solution of calcium chloride with excess of the ammonium salt. It is insoluble in water.

Phosphato-chlorides of calcium are obtained by evaporating solutions of tricalcium phosphate in hydrochloric acid. A saturated solution, on spontaneous evaporation, deposits rhomboidal plates of $7CaH_4(PO_4)_2{\cdot}CaCl_2,14H_2O$. If the solution is evaporated over the water-bath, dicalcium phosphate is first deposited, then, on further evaporation, the above phosphatic chloride comes down, and afterwards white scales of $CaH_4(PO_4)_2{\cdot}CaCl_2,H_2O$. When a solution of dicalcium orthophosphate in hydrochloric acid is saturated at ordinary temperatures with tricalcium phosphate, then mixed with half the quantity of hydrochloric acid already contained in it, and evaporated, on cooling below 6° crystals separate out of the composition

$$4CaH_4(PO_4)_2{\cdot}CaCl_2,8H_2O$$

(Erlenmeyer, *J.* 1857, 146).

Calcium silico-phosphate. According to Carnot and Richard (Compt. rend. 97, 316), the brownish-black slag, formed in working the Thomas-Gilchrist process at Joeuf (Meurthe-et-Moselle), is covered with black crystals, some slender needles, others right rhombic prisms with brilliant faces, frequently aggregated in columnar masses terminating in vitreous, translucent, blue crystals. Similar blue crystals are found in the cavities, possessing the constant composition $8P_2O_5{\cdot}8SiO_2{\cdot}Al_2O_3{\cdot}FeO{\cdot}36CaO$, essentially a calcium silico-phosphate

$$Ca_3(PO_4)_2 + Ca_2SiO_4.$$

Calcium arsenates. Dicalcium arsenate occurs native as *haidingerite* $Ca_2H_2(AsO_4)_2,H_2O$, and *pharmacolite* $Ca_2H_2(AsO_4)_2,5H_2O$, and may be prepared by adding a solution of disodium arsenate to excess of calcium chloride. The tetrahydric arsenate obtained by addition of lime water to arsenic acid is soluble, while the tricalcium arsenate is insoluble in water, and may be prepared by precipitating calcium chloride with trisodium arsenate. On evaporating a hydrochloric acid solution of calcium ammonium arsenate with platinum chloride, the mass left on ignition of the platinochloride is found to contain fine white prisms of the tricalcium orthoarsenate $Ca_3(AsO_4)_2$ insoluble in acids. The metaarsenate $Ca(AsO_3)_2$ is formed as an insoluble crystalline powder when mixtures of arsenious anhydride and calcium carbonate are ignited.

Calcium ammonium arsenate

$$CaNH_4AsO_4,7H_2O$$

is produced by mixing a hot solution of arsenic acid in excess of ammonia with calcium nitrate or chloride, when it crystallises on cooling in tables. In a vacuum over sulphuric acid, they become $Ca_3(NH_4)H_2(AsO_4)_2,3H_2O$, and when dried at 100° have the composition

$$Ca_5(NH_4)H_5(AsO_4)_6,3H_2O.$$

On ignition they are converted into calcium pyroarsenate $Ca_2As_2O_7$ (Bloxam, Chem. News, 54, 168).

Another salt, $Ca(NH_4)_2H_2(AsO_4)_2$, is obtained by adding excess of ammonia to a solution of dicalcium arsenate in nitric acid, as a flocculent precipitate, soon becoming a mass of needles. The same salt is obtained in crystals belonging to the regular system when the solution of the dicalcium salt is only partially precipitated and allowed to stand; hence it appears to be dimorphous (Baumann).

Calcium silicide was obtained by Moissan by heating calcium oxide with excess of silicon in a carbon tube by means of the electric furnace. It forms greyish crystals, sp.gr. 2·5, which are slowly decomposed by water with evolution of hydrogen.

Calcium silicates. Calcium oxide is an important base in a large number of natural silicates, and is the principal basic constituent

of the following minerals: *Wollastonite* $CaSiO_3$ or tabular spar, occurring in monoclinic crystals; *okenite* $CaH_2(SiO_3)_2,H_2O$; *xonaltite* $4CaSiO_3,H_2O$; *gurolite* $Ca_2H_2(SiO_3)_3,H_2O$; and *apophyllite* $4CaH_2(SiO_3)_2{\cdot}KF,4H_2O$.

Gorgeu (Compt. rend. 99, 256) obtained artificial wollastonite by fusing 1 gram of silica with 15 grams calcium chloride and 3 grams common salt at a cherry-red heat in a current of moist air for half an hour. On treating the product with cold water and acetic acid, a residue of long prisms of wollastonite mixed with round grains of tridymite was obtained. The artificial wollastonite possessed the same chemical and optical properties and crystalline form as the natural, but was somewhat softer, the hardness of the mineral being 5, and that of the artificial 3·5.

If molecular proportions of precipitated silica and calcium chloride are heated to a high temperature in presence of water vapour, $CaSiO_3$ is also formed, but not in form of wollastonite. With twice the amount of chloride the normal silicate Ca_2SiO_4 is formed.

Doelter (Jahrb. Min. 1886, 1, 119) found that in absence of steam, a hexagonal $CaSiO_3$ is always formed; hence wollastonite must have been formed in presence of steam. Calcium silicate is therefore dimorphous.

The silicates $2CaO{\cdot}SiO_2$, $2CaO{\cdot}3SiO_2$, $CaO{\cdot}2SiO_2$, and $CaO{\cdot}3SiO_2$ are produced by exposing mixtures of quartz and marble in these proportions to the heat of a smith's forge. The last three are the most fusible.

On precipitating the solution of any calcium salt with sodium or potassium silicate, the silicates $2CaO{\cdot}9SiO_2,3H_2O$ and $CaO{\cdot}SiO_2$ have been obtained by Lefort and Von Ammon respectively.

Gorgeu (Compt. rend. 99, 256) obtained two chlorosilicates by heating to a high temperature silica and calcium chloride in proportion of one molecule to seven in presence of water vapour. The first, $2CaO{\cdot}SiO_2{\cdot}CaCl_2$, forms birefractive rhombic plates. The second, $CaO{\cdot}SiO_2{\cdot}CaCl_2$, forms hexagonal plates, and is produced more rapidly than the former, which requires prolonged heating. Both compounds are decomposed by water.

Calcium boride CaB_6 was obtained by Moissan and Williams by heating quicklime with boron in an electric furnace, and by reducing calcium borate with aluminium in the presence of carbon, then washing with hydrochloric and hydrofluoric acids and ether. It is a black crystalline body; sp.gr. 2·33. Nitric acid attacks it vigorously.

Calcium borate occurs in nature in several combinations. The best known is colemanite $HCa(BO_2)_3,2H_2O$, which crystallises in beautiful monoclinic prisms.

Calcium silicoborate $CaO{\cdot}2SiO_2{\cdot}CaB_2O_4$ occurs with one molecule of water as *datholite*, and with two molecules of water as *botryolite*. Calcium titanate or $CaTiO_3$ occurs in nature as *perovskite*.

Calcium silicotitanate $CaO{\cdot}3SiO_2{\cdot}2CaTiO_3$ occurs as *sphene*.

Calcium monosulphide CaS. Perfectly dry lime remains unaltered on passing over it a current of dry sulphuretted hydrogen; but on hydrating the lime and again passing the gas, calcium sulphide is formed:

$$Ca(OH)_2+H_2S=CaS+2H_2O.$$

The most favourable temperature is 60° (Veley, Chem. Soc. Trans. 1885, 478).

It may also be prepared by heating the sulphate with coal or charcoal, or by action of carbonic oxide at a red heat:

$$CaSO_4+4CO=CaS+4CO_2.$$

It may be prepared in the crystalline state by direct reduction of the sulphate with carbon in the electric furnace; Müller (Cent. Min. 1900, 178) has obtained it in small cubes.

Anhydrous calcium sulphide is a white powder which emits a smell of SH_2 in the air. It turns yellow on moistening, due to the formation of oxidised products. It is but sparingly soluble in water, and is decomposed by boiling water, with formation of hydroxide and sulphydrate of calcium $2CaS+2H_2O=Ca(HS)_2+Ca(HO)_2$. Suspended in water, it is readily decomposed by carbonic acid, with formation of calcium carbonate and sulphuretted hydrogen

$$CaS+H_2O+CO_2=CaCO_3+H_2S.$$

After being heated, calcium sulphide shines in the dark, and was long known as *Canton's phosphorus*.

According to Verneuil (Compt. rend. 103, 600), calcium sulphide with a violet phosphorescence may be prepared as follows: 20 grams of finely powdered lime, obtained by heating the shells of *Hypopus vulgaris*, is intimately mixed with 6 grams of sulphur and 2 grams of starch, and 8 c.c. of a solution containing 0·5 gram basic bismuth nitrate and 100 c.c. of absolute alcohol acidified with a few drops of hydrochloric acid are added. The mixture is exposed to the air until most of the alcohol has evaporated, and is then heated to cherry redness for 20 minutes. When completely cooled, the upper layer of calcium sulphate is removed, and the calcined mass powdered and again heated for 15 minutes. The violet phosphorescence of the product is due to the trace of bismuth. 0·1 p.c. of sulphides of antimony, cadmium, mercury, tin, copper, lead, uranium, platinum, or zinc imparts a bluish- or yellowish-green tint to the phosphorescence. Manganese produces an orange shade. A mixture of 100 parts lime, 30 parts sulphur, 10 of starch, and 0·035 of lead acetate yields a sulphide with a beautiful yellowish-green phosphorescence.

Pure calcium carbonate mixed with 2 p.c. sodium carbonate, and 0·02 p.c. common salt, heated with 30 p.c. sulphur and 0·02 p.c. bismuth nitrate, yields a similar product to that obtained by use of *Hypopus* shells. Pure calcium sulphide does not phosphoresce; the phenomenon is due to small quantities of impurities; thus in the last mixture it has been shown by Verneuil to be due to simultaneous presence of traces of bismuth oxide, sodium carbonate and chloride, and calcium sulphate.

These phosphorescing varieties of calcium sulphide are utilised in the manufacture of luminous paints. Abney (Phil. Mag. [5] 13, 212) found that the emission spectrum showed greatest luminosity between G and F, and a feebler one extending from between E and F as far as the red. The rays of the electric light somewhat beyond H on one side and G on the other are most active in exciting phosphorescence.

Calcium disulphide CaS_2 is deposited in yellow crystals of the composition $CaS_2,3H_2O$ from the solution obtained by boiling sulphur with milk of lime and filtering while hot.

Calcium pentasulphide CaS_5 is formed when the monosulphide or hydrate of calcium is boiled for a long time with excess of sulphur. Concentrated solutions of calcium hydrosulphide $Ca(HS)_2$ also react energetically upon powdered roll sulphur; on preventing access of air by performing the operation in a current of hydrogen, an orange-red solution is produced with fall of temperature, and on warming the calcium is completely converted into CaS_5. The reaction is reversible, a current of sulphuretted hydrogen causing deposition of sulphur and reformation of hydrosulphide.

Calcium oxysulphides. When calcium hydroxide is used as above, besides CaS_5 there is also formed an oxysulphide of the composition $5CaS{\cdot}CaO,20H_2O$ (Rose). The same substance is obtained in gold-coloured needles when the solution obtained by boiling crude calcium monosulphide with much water is evaporated.

According to Hoffmann (Compt. rend. 62, 291), a mixture of two molecules of calcium monosulphide and one molecule lime at a red heat, forms the oxysulphide $2CaS{\cdot}CaO$. This oxysulphide is contained in recently lixiviated soda residues.

Geuther (Annalen, 224, 178) obtained crystals of $CaS_3{\cdot}2CaO,10H_2O$ by boiling sulphur in milk of lime. They dissolve in hydrochloric acid, forming hydrogen persulphide H_2S_3, and a little H_2S. On boiling calcium monosulphide and sulphur with water, crystals of $CaS_3{\cdot}3CaO,15H_2O$ were obtained. Divers obtained a compound of the formula $11CaS{\cdot}5CaO$ by igniting lime in a mixture of carbon dioxide and carbon disulphide.

Calcium sulphydrate $Ca(HS)_2$ is formed together with the hydroxide when the monosulphide is boiled with water. The best mode of preparing it is to pass sulphuretted hydrogen through the hydroxide or sulphide suspended in water, with constant agitation, until it ceases to be absorbed. It is difficult to obtain in the solid state, being decomposed, when the stage of crystallisation is reached, into SH_2 and CaS which separates in silky prisms.

Divers (Chem. Soc. Trans. 1884, 270) obtained it in the solid form by forcing sulphuretted hydrogen through semi-solid calcium hydroxide and water so as to obtain a saturated solution of the sulphydrate. Air was excluded, and, on settling, decanting in a stream of H_2S, and cooling by ice, crystals formed in abundance. They were colourless prisms, melting on slight rise of temperature with partial decomposition. They readily dissolved in a fourth of their weight of water, and could not be removed from the atmosphere of sulphuretted hydrogen without decomposition. They possessed the formula

$$CaH_2S_2,6H_2O.$$

Calcium sulphydrate may be used as a depilatory. If sulphuretted hydrogen be passed into thin milk of lime till the mass acquires a bluish-grey colour, the paste thus formed, when thinly laid upon the surface from which the hair is to be removed, permits of the ready removal of the hair a minute or two afterwards by scraping with a dull knife. It has been proposed to employ it in the tan-yard.

Calcium hydroxy-sulphydrate $Ca(SH)(OH)$ is formed, according to Divers, by action of water upon the crystals of the last-described salt:

$$Ca(SH)_2+H_2O = Ca(SH)OH+H_2S.$$

Also by union of water with calcium sulphide, as in interior of heaps of soda waste; and by reaction between $Ca(OH)_2+H_2S$ in the coal-gas purifier. Exposed to air, crystals of $Ca(HS)_2$ are rapidly converted to Ca(SH)OH, and concentrated solutions of the sulphydrate exposed to air become rapidly covered with crystals, and an abundant crop of crystals of Ca(SH)OH is obtained on passing in a current of air. The crystals are colourless four-sided prisms of silky lustre, easily obtained dry, of the composition $Ca(SH)OH,3H_2O$. They slowly evolve SH_2 in air, and become yellow by absorption of oxygen. They are readily soluble in water, but the solution rapidly decomposes into hydroxide and sulphydrate. They are insoluble in alcohol.

According to Folkard (Chem. News, 49, 258), by exposing calcium hydroxide to the action of sulphuretted hydrogen until it ceases to gain weight a grey powder of the composition $4Ca(HO)_2{\cdot}3H_2S$ is obtained. By the action of coal gas sulphuretted hydrogen is evolved from it, and at 100° water is eliminated, leaving

$$Ca(OH)_2{\cdot}Ca(SH)OH.$$

This greyish-green powder, when gently heated in coal gas, leaves a yellowish-white salt

$$2Ca(HO)_2{\cdot}Ca(SH)OH{\cdot}CaS,$$

and this at a red heat forms $2CaO{\cdot}Ca(SH)OH{\cdot}CaS$, which, when ignited in air, burns like tinder to $CaSO_4$.

Calcium sulphocarbonate $CaCS_3$. Lime over which coal gas containing sulphuretted hydrogen has been passed readily absorbs carbon disulphide. Absorption is most complete when the lime is moistened with water; this material, when fouled, is mixed with an equal weight of slaked lime. The absorption of carbon disulphide stops when one-third of the sulphide is converted to sulphocarbonate $CaS+CS_2 = CaCS_3$. On exposing the product for a short time to the air, it is again rendered capable of removing carbon disulphide.

On passing hydrogen saturated with vapour of carbon disulphide into a mixture of calcium monosulphide and a little water, the liquid becomes red, and *in vacuo* deposits red prismatic very deliquescent needles of composition

$$Ca(OH)_2{\cdot}CaCS_3,7H_2O.$$

When the hydroxy-sulphydrate is employed instead of monosulphide, yellow crystals of

$$2Ca(OH)_2{\cdot}CaCS_3,10H_2O$$

are obtained.

From these facts Veley (Chem. Soc. Trans. 1885, 478) concludes that the carbon disulphide is absorbed by Ca(SH)OH, and not by CaS, and that the reactions are as follows:—

(1) $CaS+H_2O = Ca(SH)OH.$

(2) $Ca(SH)_2+H_2O = Ca(SH)OH+H_2S.$

(3) $2Ca(SH)OH+CS_2 = Ca(OH)_2{\cdot}CaCS_3+H_2S.$

The basic sulphocarbonate is unstable, being decomposed slowly by sulphuretted hydrogen and readily by carbon dioxide.

When milk of lime is agitated with carbon

disulphide, bright orange needles of a basic sulphocarbonate $Ca(HO)_2 \cdot CaCS_3, 6H_2O$ are deposited.

Calcium selenides. The monoselenide is formed as a flesh-coloured precipitate by precipitating calcium chloride with potassium monoselenide. Lime water saturated with seleniuretted hydrogen deposits crystals of calcium selenide when exposed to the air. When lime and selenium are heated just below redness, a polyselenide mixed with calcium selenite is formed.

Calcium sulphite $CaSO_3$ is formed when a solution of an alkaline sulphite is added to the solution of a calcium salt: it is a white powder soluble in 800 parts of water. It dissolves in sulphurous acid, and the solution on exposure to air deposits six-sided needles of the composition $CaSO_3, 2H_2O$.

The solution in sulphurous acid is known commercially as bisulphite of lime, and is manufactured by passing sulphur dioxide into milk of lime. In Kynaston's process (Pat. 15659, 1884) a mixture of calcium chloride solution, magnesia, and a little carbonate of lime is brought into contact with sulphur dioxide. The SO_2 is caused to ascend a flagstone tower packed with pigeon-holed brickwork, while the mixture is allowed to run down the tower in such proportions, that from the base there runs a mixture of neutral calcium sulphite, suspended in a solution of magnesium chloride containing the excess of sulphurous acid. The sulphite is settled out in tanks, the supernatant liquor drawn off and concentrated to 40°–45°Tw.; then a quantity of alkali waste is added to it in a closed iron vessel, and the whole heated, when sulphuretted hydrogen is given off, and calcium chloride, magnesia, and calcium carbonate with alkali cinders remain. The latter are removed in a strainer, and the emulsion is ready to be again treated with sulphur dioxide. The whole of the calcium carbonate present is converted to sulphite, carbon dioxide being evolved.

According to Birnbaum and Wittich (Ber. 13, 651), calcium oxide does not absorb sulphur dioxide gas below 400°, but at this temperature combination takes place rapidly with formation of a basic sulphite $Ca_6S_5O_{16}$ or $6CaO \cdot 5SO_2$. At 500° the gas is rapidly absorbed, but the sulphite splits up into sulphate and sulphide.

Calcium sulphate $CaSO_4$ is frequently found in limestone rocks or in company with common salt in the anhydrous state as the mineral *anhydrite*. Anhydrite occurs both in rhombic crystals and in a semi-crystalline massive form. More frequently the sulphate is found hydrated as *gypsum* $CaSO_4, 2H_2O$, of which the well-crystallised form is termed *selenite*, a fibrous variety *satin-spar*, and a finely crystallo-granular form *alabaster*. Selenite occurs in fine monoclinic prisms, frequently twinned in characteristic arrow-head shapes.

The anhydrous sulphate may be artificially obtained in crystals resembling anhydrite, of sp.gr. 2·9, by fusing calcium chloride with excess of potassium sulphate (Manross, J. 1852, 9).

Hydrated calcium sulphate is precipitated on adding dilute sulphuric acid or a soluble sulphate to an aqueous solution of calcium chloride. The sp.gr. of gypsum is 2·31. When it is heated to 100°–120° it gives up three-fourths of its water rather quickly, but it requires a temperature of 200°–250° to expel the remainder. Dried at 100°, the hydrate $2CaSO_4, H_2O$ of sp.gr. 2·7 is left. The anhydrous salt fuses at a red heat without decomposition, and on cooling, assumes the structure of anhydrite. When dehydrated calcium sulphate is pulverised and mixed with water, it absorbs two molecules of water, and solidifies to a very hard mass with evolution of heat, expanding in so doing so as to fill any mould in which it is cast; hence the use of gypsum or plaster of Paris in preparing casts. If the gypsum has been heated to a little over 200°, thus being deprived of all its water, it becomes dead burnt, and takes up water very slowly and without hardening.

Plaster of Paris is prepared very extensively on the large scale by burning gypsum. Its good qualities mainly depend upon the choice of raw material—heavier and denser varieties yielding the best commercial results—and upon the mode of burning. The lowest temperature at which gypsum can be advantageously burnt is 80°, but a temperature of 110°–120° gives the best technical results. As a rule also, the smaller the pieces, the more homogeneous the product.

It is burnt in kilns or ovens, taking precautions not to permit the fuel to come in contact with it so as to reduce it to sulphide. The walls of the kilns are of strong masonry, spanned by a ventilated arch. The interior is divided into two parts—an upper larger chamber for reception of the gypsum, and a lower series of small fire chambers beneath, where brushwood or coke is burnt to obtain the required temperature. In Scanegatty's oven the interior is divided by an arch about a foot from the floor, upon the under side of which play the flames from a furnace connected with a lower chamber, the hot air and gases passing afterwards through apertures into the gypsum chamber. The aqueous vapour passes away by a chimney at the top of the oven.

Dumesnil's oven is a form which has been much employed; it differs from Scanegatty's in the peculiar arrangement of the lower fire-room, which has twelve openings, the lower blocks of gypsum being arranged so as to facilitate the circulation of the draught from these. The firing is continued for about 4 hours, then the heat is increased for 8 hours, when all openings are closed, and 5–6 cubic metres of coarse gypsum powder spread equally over the top of the burning sulphate. By this means considerable saving of fuel is effected. After standing 12 hours to cool, the contents of the kiln are removed. It is mostly in state of powder, and the pulverisation is completed by grinding in a stamp or roller mill. The powder is then sifted and stored in a dry place.

Many improvements on the old forms have been effected by making the furnaces continuous, and so designing them that the gypsum is equally heated, and, consequently, dehydrated throughout. This end is also ensured by grinding the gypsum before calcination. The types of ovens employed are very numerous. That of Petry and Hecking, Dortmund, is a rotary kiln, with mill and furnace arranged similarly to those of a cement works. The barrel oven of Perin of Paris is a revolving cylinder, supported upon hollow trunnions, one of which serves for the

entrance of the heated gases from the furnace, and the other for exit. The charging is performed from a hopper placed above through a trap-door in the side of the cylinder, which similarly serves to discharge the material when burnt. Other ovens are made stationary, but are provided with revolving screws or vanes, which serve to keep the ground gypsum in constant motion, and also to discharge it. Some ovens are heated by means of steam. In burning gypsum for ordinary plaster work, the mineral is used in lumps, and the temperature employed is considerably higher than for finer qualities of stucco. Where a harder plaster is required capable of giving a polish, the burnt gypsum is soaked in alum and reburnt before grinding.

Calcium sulphate cements. Gypsum, hydrated calcium sulphate $CaSO_4,2H_2O$, is the source of this class of cements, which depend for this property of setting on the reacquisition of the water associated with calcium sulphate in gypsum.

The chemistry of calcium sulphate cements, though much the simplest of that concerned with cements depending for their setting on hydration, is of considerable difficulty, and its present condition is far from definitive. Putting aside controversial views, the situation may be summarised thus: When $CaSO_4,2H_2O$ is heated, it loses water, and at a temperature of about 107° becomes converted into the hemi-hydrate $2CaSO_4,H_2O$. When this substance is mixed with water, it is hydrated, and reforms $CaSO_4,2H_2O$, which crystallises first in the orthorhombic, and finally in the monoclinic, system. The quantity of water sufficient to bring the hemi-hydrate back to the fully hydrated condition is much smaller than is necessary to dissolve it; but, nevertheless, complete crystallisation is accomplished thus: the hemi-hydrate readily forms a supersaturated solution, from which not it but the dihydrate is deposited. The water thus released dissolves another portion of the hemi-hydrate, and the process of deposition is repeated indefinitely until, provided there was originally enough water to transform $2CaSO_4,H_2O$ into $CaSO_4,2H_2O$, the whole of the former will have been dissolved in detail and deposited in detail in the shape of the latter. As stated in the section dealing with Portland cement, it is believed that this formation of a supersaturated solution, deposition of the surplus dissolved material, and re-use of the water for the solution of another fraction of the material is general for cements which set when mixed with water, and, although there are many gaps in the proof, yet the hypothesis is useful. In the case of calcium sulphate cements, it may be regarded as well established.

The hemi-hydrate $2CaSO,H_2O$, constitutes plaster of Paris. If gypsum is heated to a higher temperature, *e.g.* above 130°, it becomes completely dehydrated, and yields $CaSO_4$. It appears that $CaSO_4$ can exist in two or more modifications, which behave differently with water As all eventually become hydrated, but not all will set as plaster of Paris, it is probable that only those which will set possess the characteristic property of forming a supersaturated solution, and allowing the mass to crystallise in stages in the manner described above. Keene's cement and Estrichgips (flooring plaster) are examples of cements consisting substantially of anhydrous calcium sulphate. Their setting is influenced by both the temperature at which they have been burnt and by the presence in them of small quantities of substances other than $CaSO_4$, the *modus operandi*, of which is exceedingly obscure. In whatever way they are prepared, the final product of setting is $CaSO_4,2H_2O$.

The manufacture of plaster of Paris is conducted by heating the mineral gypsum to a temperature above that necessary to remove

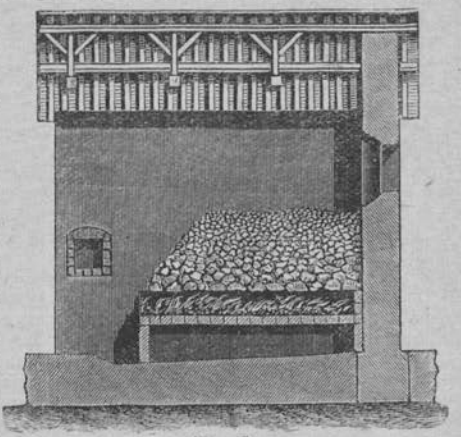


FIG. 8.

$\frac{3}{4}$ of its water of crystallisation, and below that requisite to dehydrate it completely. Several methods of burning are in use, ovens, kettles, and rotatory kilns being employed. In English practice a simple oven of the kind shown (Figs. 8 and 9) is adopted, the gypsum in lumps being piled on arches in which the fuel is burnt. In

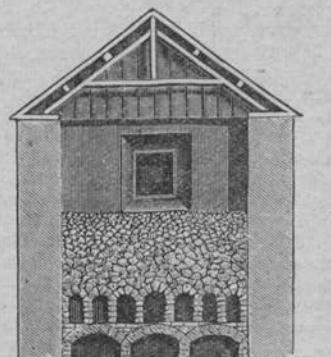


FIG. 9.

the United States the common plan is to grind the gypsum first, and heat it in a large iron pot on kettle set in brickwork and heated from below. During the process the powdered material is stirred by an agitator driven by power. The most modern method is to burn

the roughly crushed material in a rotatory calciner, heated externally so as to present contact with the fuel, the product like that made in ovens needing to be ground after burning is complete. In all cases the temperature must be carefully regulated so that only the hemihydrate is obtained. On account of the fact that a considerable quantity of water has to be driven off, the temperature of the source of heat may be and in practice is considerably higher than 107°, but the temperature of the mass of gypsum must not be allowed to rise above this, lest complete dehydration occur.

Plaster of Paris varies in composition according to the purity of the gypsum from which it is made. The following analyses are illustrative, and for comparison the composition of the hemihydrate is appended :—

	$2CaSO_4,H_2O$	Commercial plaster of Paris	
		1	2
	p.c.	p.c.	p.c.
Calcium sulphate ($CaSO_4$)	93·8	94·53	83·55
Water (H_2O)	6·2	4·12	6·67
Silica (SiO_2)	—	—	4·27
Alumina and ferric oxide ($Al_2O_3+Fe_2O_3$)	—	0·57	0·47
Calcium carbonate ($CaCO_3$)			3·07
Magnesium carbonate ($MgCO_3$)	—	—	1·47

Keene's cement is usually made in this country by first burning the gypsum to the condition of plaster of Paris, dipping the lumps in a solution of alum or of aluminium sulphate, and reburning at a temperature of about 500°, the operation being conducted in ovens in which the fuel is prevented from coming into contact with the material, so as to avoid discolouration. The following is a typical analysis of Keene's cement of good quality :—

	Per cent.
Silica (SiO_2)	trace
Alumina (Al_2O_3)	trace
Lime (CaO)	42·04
Magnesia (MgO)	trace
Sulphuric anhydride (SO_3)	56·54
Carbonic anhydride (CO_2)	1·37

It will be seen that Keene's cement is almost chemically pure $CaSO_4$, the quantity of added matter, such as alum, being negligible. As mentioned above, the function of this and similar additions is obscure, and even the necessity for their use appears doubtful because flooring plaster (*Estrichgips*) is made by burning pure gypsum at about 500°, and, though destitute of alum and the like, sets well.

There are many different qualities of plaster, but all are of the type of plaster of Paris, or of Keene's cement. The former set in a few minutes, whilst the latter take several hours, and as the rate of setting of plaster of Paris is inconveniently rapid for some purposes, 'retarders,' consisting of such organic substances as glue, blood, and vegetable juices, are often added. These substances of a colloidal nature probably act by obstructing the growth of the crystals of $CaSO_4,2H_2O$, and thus delaying the process of hydration, and, consequently, the setting.

The chief uses of plasters made from calcium sulphate is for making castings or mouldings for interior decoration, for which their white colour, conspicuous in the purer kinds, and their expansion on setting and causing the production of sharp outlines, peculiarly adapt them. On account of the solubility of calcium sulphate in water, these plasters cannot be used for outdoor work. Minor uses are for making moulds for any material which can be cast at a sufficiently low temperature, for making surgical support for broken limbs, and, as an addition to Portland cement, to lengthen its time of setting.

Calcium sulphate is very slightly soluble in water, the anhydrous sulphate being nearly insoluble. The solubility of the hydrate attains a maximum at 35°, one part dissolving in 393 parts water (Poggiale); at 0° in 488 parts, and at 100° in 460 parts. The solubility is increased by presence of hydrochloric or nitric acids, or chlorides of ammonium or sodium, hence its presence in salt springs; probably in most cases partial double decomposition has occurred.

According to Lunge (J. Soc. Chem. Ind. 1885, 31), the solubility of calcium sulphate in solutions of sodium chloride increases with the percentage of salt, but diminishes with increase of temperature.

At 21·5°, 100 c.c. of a 3·53 p.c. solution of NaCl dissolves 0·5115 gram $CaSO_4$.

At 18·0°, 100 c.c. of a 14·18 p.c. solution of NaCl dissolves 0·7340 gram $CaSO_4$.

At 101·0°, 100 c.c. of a 3·53 p.c. solution of NaCl dissolves 0·4891 gram $CaSO_4$.

At 102·5°, 100 c.c. of a 14·18 p.c. solution of NaCl dissolves 0·6248 gram $CaSO_4$.

Calcium chloride diminishes the solubility of $CaSO_4$ the more it is concentrated, but at the boiling-point the concentration is immaterial. Hydrochloric acid increases the solubility both with increase of concentration and of temperature.

Gypsum is readily soluble in excess of sodium thiosulphate, forming calcium thiosulphate, which combines with the excess of the sodium salt to form a soluble double thiosulphate. On addition of alcohol, this double salt separates as a thick heavy liquid, which solidifies, forming needle-shaped crystals.

Acid calcium sulphate $CaSO_4\cdot H_2SO_4$ is formed by heating the neutral sulphate with strong sulphuric acid to 80°–100°. A portion of the porous mass produced dissolves and separates on cooling in microscopic prisms of the composition above indicated. It is decomposed by water, even the moisture of the air, into gypsum and sulphuric acid.

Calcium-sodium sulphate $CaNa_2(SO_4)_2$ occurs native in rhombic prisms as the mineral *glauberite*. It may be obtained in the same form by fusing together calcium and sodium sulphates. On heating 50 parts sodium sulphate (Glauber's salt) with an emulsion of 1 part gypsum in 25 parts water to 80°, crystalline needles of

$$CaSO_4\cdot 2Na_2SO_4,2H_2O$$

are deposited. On further heating, these crystals are transformed into microscopic rhombohedral crystals of glauberite.

In the Welsh process of manufacturing sodium acetate, during evaporation of the liquor formed by double decomposition of calcium acetate by sodium sulphate, micaceous spangles of glauberite have been noticed by Folkard (Chem. News, 43, 6) to separate out. This

explains why calcium sulphate so tenaciously retains sodium sulphate.

Calcium potassium sulphate

$$CaSO_4 \cdot K_2SO_4, H_2O$$

occurs native in monoclinic crystals as *syngenite*. It is formed by mixing solutions of the two salts. When a mixture of equal weights of anhydrous calcium sulphate and potassium sulphate is stirred up with less than its weight of water, the mass suddenly solidifies. If 4–5 parts of water are used, the solidification is not quite so rapid, but gives casts superior to those of plaster of Paris, inasmuch as they possess a polished surface.

A salt of the composition

$$CaSO_4 \cdot KNH_4SO_4, Aq.$$

is obtained by adding an excess of potassium sulphate to a warm concentrated solution of ammonium sulphate which has been saturated with calcium sulphate. The same salt is formed when the double sulphate of calcium and potassium is treated with a warm solution of ammonium sulphate (Fassbender, Ber. 11, 1968).

Calcium thiosulphate $CaS_2O_3, 6H_2O$ is prepared by heating an emulsion of calcium sulphate and sulphur in water.[1] It forms triclinic prisms soluble in their own weight of cold water. On heating the solution to 60°, it is decomposed with deposition of sulphur. It is used for the preparation of antimony cinnabar Sb_2OS_2, used in oil painting.

Calcium chromate $CaCrO_4, 4H_2O$ is prepared by dissolving calcium carbonate in aqueous chromic acid, or as a light-yellow precipitate on mixing concentrated solutions of calcium chloride and potassium chromate. Bourgeois (Jahrb. Min. 1880, 1 Ref. 351) prepares the anhydrous salt by heating to bright redness two molecules of the chloride with a molecule of potassium chromate and one of sodium carbonate. It forms slender yellow needles, formed from a rectangular prism, moderately soluble in water, and is used as a pigment. The hydrated salt gives up its water at 200°.

The acid chromate $CaCr_2O_7, 3H_2O$ is obtained in red deliquescent crystals by evaporating a solution of the neutral salt in aqueous chromic acid.

Calcium potassium chromate $(CaK_2)(CrO_4)_2Aq.$ forms yellow silky needles, obtained by saturating acid potassium chromate with calcium hydroxide.

Detection and Estimation of Calcium.—The hydrated chloride, when heated in a non-luminous flame on platinum wire, imparts to the flame a red colour of less brilliancy than strontium, but still very distinct. If the compound to be tested is decomposed by hydrochloric acid, it is only necessary to moisten the platinum wire with the acid, and then dip it into the powdered substance. If the compound is a silicate, it should be powdered and mixed with ammonium fluoride, gently heating on platinum foil until the fluoride is volatilised; it is then moistened with sulphuric acid and tested in the flame on platinum wire, when the red colouration is obtained as soon as the excess of acid is driven off.

The spectrum of this red flame consists of a large number of lines, of which the green line Caβ is most prominent. Another characteristic line is the strong orange one Caα. A quantity of calcium chloride as little as $\frac{5}{100000}$ mgm. may be detected by the spectroscope.

All the calcium salts except the sulphate dissolve readily in nitric or hydrochloric acid; the carbonate, phosphate, arsenate, and oxalate are insoluble, the sulphate sparingly, and almost all the other salts of calcium are readily soluble in water.

Ammonium carbonate precipitates calcium carbonate from solutions of calcium salts, thus separating it from the alkali metals. In order to completely remove calcium (the carbonate being slightly soluble, 1 part dissolving in 40,000 parts water), it is usual to precipitate it by means of ammonium oxalate in ammoniacal solution, calcium oxalate being almost completely insoluble in water. It is distinguished from barium and strontium by the greater solubility of its sulphate, a solution of calcium sulphate giving an immediate precipitate with barium salts, and one after some time with soluble strontium salts.

Calcium is generally estimated quantitatively as oxide or carbonate with intermediate precipitation as oxalate, by addition of ammonia till the reaction is alkaline, and afterwards of ammonium oxalate. The washed and dried oxalate is heated to low redness if it is to be converted into carbonate; but if the oxide is required it is ignited over the blowpipe in a platinum crucible. If boric or phosphoric acids are present, this method cannot be employed, and the calcium is then precipitated as sulphate by adding dilute sulphuric acid and alcohol. Phosphoric acid may also be first eliminated by adding ferric chloride and separating the iron and phosphoric acid by precipitation with ammonia and ammonium acetate. The calcium may then be estimated in the filtrate in the usual way.

If strontium or barium are present in small amounts, the weighed calcium oxide is dissolved in nitric acid, evaporated to dryness, and equal parts of alcohol and ether added. The calcium nitrate dissolves and barium and strontium fall as a crystalline precipitate.

In presence of much magnesium Sonstadt (Chem. News, 29, 209) recommends use of potassium iodate, which completely precipitates calcium, but not a trace of magnesium. G. S. B.

CALCULI *v.* URINE.

CALICHE. The term by which the impure native sodium nitrate or Chili saltpetre is known throughout South America. Also applied to a limestone hardpan found in Arizona and elsewhere (*v.* SODIUM).

CALLUTANNIC ACID *v.* TANNINS.

CALMATAMBIN *v.* GLUCOSIDES.

CALOMEL. *Mercurous chloride* (*v.* MERCURY).

CALOPHYLLUM INOPHYLLUM (Linn.). A tree (ord. *Guttiferæ*), Alexandrian laurel, dilo of Fiji, tamarind of E. Polynesia, and sultana champa (Hind.) of India), the seeds of which yield 60 p.c. of a fragrant green oil, fluid at ordinary temperatures, solidifying when cooled below 10°. The tree bears fragrant white flowers. The oil, the woondel or bitter oil of

[1] Divers (Chem. Soc. Trans. 1884, 270) obtains it by oxidation of calcium sulphydrate in a current of air, calcium hydroxysulphydrate being first formed and then oxidised by the SH_2 to thiosulphate

$$Ca(SH)OH + 2O_2 + H_2S = CaS_2O_3 + 2H_2O.$$

Indian commerce, used for medicine and for lamp oil, is of a greenish tint, and a very little imparts its colour to a whole cask of cocoa-nut oil (Pharm. J. [3] 8, 363).

CALOTYPE *v.* PHOTOGRAPHY.

CALUMBA. *Colombo, Columbo, Radix Calumbæ.* (*Racine de Colombo*, Fr.; *Kalumba or Columbowurzel*, Ger.)

The root of the *Jateorhiza Columba* (Miers), a herbaceous climbing plant, inhabiting the forests of Eastern Africa (Flück. a. Hanb. 23; Bentl. a. Trim. 13). The fleshy root is sliced transversely and dried. It was introduced into Europe in the 17th century as an antidote for poison, and found a place in the London Pharmacopœia of 1788. It possesses mild bitter tonic properties, for which purpose it is now chiefly employed in medicine.

Proximate analyses of calumba were made by Planche (Bl. Ph. 3, 189) and Buchner (Ph. C. 1831, 429). It consists of *bitter matter*, 10–13 p.c.; *yellow resinous extractive*, 5 p.c.; *volatile oil*, traces; *starch*, 30–35 p.c.; *gum*, 4–9 p.c.; and *woody fibre*, 12–39 p.c. The *ash* is about 6 p.c. Tannic acid is absent.

The following physiologically active constituents have been isolated from calumba root. *Columbin*, a bitter principle, discovered in 1830 by Wittstock and obtained by recrystallisation of the ethereal extract of the roots from glacial acetic acid. It forms colourless prisms, m.p. 182°, insoluble in hot or cold water, and in cold alcohol or ether, readily in hot ether, chloroform, or alcohol. When boiled with caustic potash and a small amount of water in a current of hydrogen, columbic acid, m.p. 220°, is formed (Frey, Annalen, 351, 372). Bödeker (*ibid.* 69, 39) detected *berberine* and a further yellow colouring agent, *columbic acid*, in the root; but from the work of subsequent investigators (Gadamar, Arch. Pharm. 240, 450; Feist, *ibid.* 245, 586), it appears that the root does not contain berberine; but that three alkaloids are present—*columbamine, jateorrhizine*, and *palmitine*—which closely resemble berberine. Ulrich (Annalen, 351, 363) has shown that columbic acid is not present in calumba root, but is formed when the partially extracted root is treated with aqueous alkali. Feist (*l.c.*) also describes a further *bitter principle* in addition to columbin, which crystallises in prisms, melting at 246° with decomposition. A. S.

CAMELINE OIL, *Dodder oil*, or *German Sesamé oil*, is prepared from the seeds of *Myagrum sativum* (Crz.), *Camelina sativa* (Linn.), ('gold of pleasure'). Several centuries ago the seed was grown all over Germany as a crop, but at present it is only cultivated on a small scale in some parts of South Germany, Belgium, Holland, Hungary, the Balkan States, and South Russia. The seed is occasionally expressed in Hull, but mostly the press cakes arrive in this country from Odessa, and are used (in Liverpool) in the manufacture of 'compound cakes.' The average composition of cameline seed is stated as follows:—

Oil	29·4 p.c.
Water	7·5 „
Albuminoids	25·9 „
Carbohydrates	17·3 „
Crude fibre	10·5 „
Ash	9·2 „

The oil has a golden-yellow colour and a pungent taste and smell. On exposure to the air it dries slowly. It is a semi-drying oil, and therefore yields, on boiling with litharge or manganese, a slowly drying varnish. The low saponification value of the oil points to the presence of erucic acid.

The 'cold-drawn' oil is used for edible purposes in Russia. The oil expressed in this country, as also the oil expressed in the hot in Hungary and the south of Russia, is used for soap making. J. L.

CAMPEACHY WOOD *v.* LOGWOOD.

CAMPHANIC ACID *v.* LACTONES.

CAMPHENE, CAMPHINE *v.* TERPENES.

CAMPHOL *v.* CAMPHORS.

CAMPHOPHORONE *v.* KETONES.

CAMPHORS. Camphors are volatile oxygenated hydrocarbons, possessing a peculiar characteristic odour. They are mostly crystalline solids, insoluble in water, but soluble in alcohol. Except in the case of a few, which are produced artificially, they are obtained from plants, where they occur associated with hydrocarbons, from which they are probably derived. Most plants when distilled with steam yield volatile oils composed of heavier oxidised compounds held in solution more or less by lighter hydrocarbons. The former often separate in crystals during the condensation of the oil or afterwards on standing, or they may be obtained by fractional distillation. Most of these oxygenated products, which are very numerous in the vegetable kingdom, and which include nearly all the 'stearoptenes' or solid portions of volatile oils, are camphors in a wide sense of that term. In a narrower meaning the word denotes the well-known laurel camphor of Japan and Formosa, the older camphor of Borneo and Sumatra, and a few other varieties. The earlier Chinese and Arabian notices of camphor refer to the Borneo variety, laurel camphor being a product of a later though unascertained period. Garcia d'Orta mentions the latter as well known in Europe in 1563, and points out, what indeed is true at the present day, that the much more costly Borneo or Sumatra camphor is entirely consumed in the East (*cf.* Flück. a. Hanb. 510).

The more important camphors, using the term in its larger signification, may be considered in four groups as isomerides or homologues of: (1) Peppermint camphor, menthol $C_{10}H_{20}O$; (2) Borneo camphor, borneol $C_{10}H_{18}O$; (3) laurel camphor $C_{10}H_{16}O$; and (4) thyme camphor, thymol $C_{10}H_{14}O$. For the most part camphors behave like alcohols or phenols, but laurel camphor and the compound menthone are ketones. Just as ketones when reduced by nascent hydrogen yield secondary alcohols, so laurel camphor is converted into borneol, and menthone into menthol.

Peppermint camphor. *Menthol* $C_{10}H_{19}\cdot OH$. The volatile oils of *Mentha piperita* (Linn.) and *M. arvensis* (Linn.), varieties *piperascens* and *glabrata*, consist of the stearoptene, menthol, together with an elæoptene, which, in the case of the English oil, is a mixture of isomeric and polymeric terpenes (Flückiger and Power, Pharm. J. [3] 11, 220), and in that of the Japanese is chiefly menthone $C_{10}H_{18}O$ (Beckmann, Jahresb. Pharmak. 1887, 363). The proportion of menthol in the Chinese and Japanese oils is so great that they

are solid at ordinary temperatures, whilst from the English and American oils only comparatively small quantities can be obtained (*cf.* Todd, Pharm. J. [3] 16, 842). The camphor is extracted either by application of cold and removal of the liquid which adheres to the precipitated mass of crystals by expression, or the oil is submitted to fractional distillation. Compare Dumas (Annalen, 6, 252); Blanchet and Sell (*ibid.* 6, 291); Walter (*ibid.* 28, 312; 32, 288); Kane (Phil. Mag. 16, 418; Annalen, 32, 285); Oppenheim (Annalen, 120, 351); Beckett and Wright (Chem. Soc. Trans. 29, 1); Atkinson and Yoshida (*ibid.* 41, 50); and Moriya (*ibid.* 39, 77). According to Trimble, the menthol of the English and American oils *pipmenthol* is not identical, but differs physically from that of the oils of China and Japan (Amer. J. Pharm. 1884, 405; *cf.* Long, Amer. Chem. J. 14, 149).

Menthol crystallises in prisms resembling magnesium sulphate. It has the odour and taste of peppermint. M.p. 36° (Opp.); 42° (B. and W., A. and Y.). B.p. 210° (Opp., B. and W., A. and Y.). Sp.gr. 15°, 0·890 (M.). Lævorotatory (Opp.; Arth, Ann. Chim. Phys. [6] 7, 438; Kanonnikoff, J. pr. Chem. [2] 31, 348). Heat of combustion (Luginin, Ann. Chim. Phys. [5] 23, 387). Menthol is very slightly soluble in water, but soluble in alcohol, ether, carbon disulphide, light petroleum, glacial acetic acid, and concentrated hydrochloric acid. It rotates on the surface of water in a similar manner to laurel camphor. Mixed with chloral, thymol, or laurel camphor, menthol reacts, forming a liquid (Kyle, Amer. J. Pharm. 1885, 429; Becker, *ibid.* 1886, 283). When menthol is boiled with a mixture of sulphuric acid diluted with half its volume of water, it changes to a deep-blue colour (Brit. Pharm. 1898).

Treated with phosphorus pentoxide menthol loses a molecule of water and forms the liquid hydrocarbon *menthene* $C_{10}H_{18}$ (W.). Concentrated hydrochloric acid (Opp.) or phosphorus pentachloride converts it into *menthyl chloride* $C_{10}H_{19}Cl$ (W.); *menthyl carbonate* $(C_{10}H_{19}O)_2CO_2$ (Arth, Ann. Chim. Phys. [6] 7, 469); *menthyl silicate* $(C_{10}H_{19}O)_4SiO_4$ (Hertkorn, Ber. 18, 1695). A nitro- derivative is formed by the action of concentrated nitric acid, which, reduced with nascent hydrogen, yields *menthylamine* $C_{10}H_{19}\cdot NH_2$ (M.). Menthol reacts with acetic acid, producing *menthyl acetate* $C_{10}H_{19}\cdot OAc$ (Opp.; Menschutkin, J. Russ. Phys. Chem. Soc. 13, 567), and with benzoic acid forming *menthyl benzoate* $C_{10}H_{19}\cdot OBz$ (Arth, Ann. Chim. Phys. [6] 7, 479). Two atoms of hydrogen are removed by treatment with chromic acid, and the liquid *menthone* $C_{10}H_{18}O$ is formed. According to Beckmann (Jahresb. Pharmak. 1887, 363), menthone is the chief liquid constituent of Japanese oil of peppermint. This compound is related to menthol in the same manner that laurel camphor is to borneol, and can be converted into menthol by the action of sodium and carbon dioxide, just as laurel camphor is converted into borneol (A. and Y.). Menthol has been obtained synthetically by Haller and Martine (Compt. rend. 140, 130).

Menthol is gradually coming more into use in medicine. It sometimes takes the place of cocaine in the production of local anæsthesia, and it is employed in certain skin diseases (*v.* OILS, ESSENTIAL).

Borneo and allied camphors. *Malayan, Barus or Dryobalanops Camphor; Borneol, Camphol,* $C_{10}H_{17}\cdot OH$. This camphor occurs naturally in dextrorotatory and lævorotatory varieties, the common borneol being the dextrorotatory form. It is the product of the *Dryobalanops aromatica* (Gärtn.), a majestic tree indigenous to Sumatra, Borneo, and Labuan, where it often rises without a branch to a height of 150 feet, when its summit is crowned by a magnificent display of foliage 50–70 feet in diameter, supporting beautiful white odoriferous flowers (Flück. a. Hanb. 516). The camphor is deposited in crystals in fissures in the old wood, and to obtain it the trees have to be sacrificed. The tree is cut down and the longitudinal fissures opened and the camphor removed. The yield is not more than from 3 to 11 lbs. from large trees. Owing to the reckless manner in which the trees have been destroyed without the planting of others, the forests of Sumatra now contain few that are worth working (Pharm. J. [3] 12, 83). The camphor is best purified by sublimation (Flück. a. Hanb.; Pelouze, Annalen, 40, 326).

Borneol is also a constituent of the following volatile oils: Rosemary, *Rosmarinus officinalis* (Linn.); (Bruylants, J. 1879, 944; Flück. a. Hanb. 489); Serpentary root, *Aristolochia serpentaria* (Linn.), (Spica, Gazz. chim. ital. 17, 314), and in Spanish lavender oil (Charabot, Bull. Soc. chim. [3] 17, 380). Besides these natural sources, borneol may be obtained by the action of reducing agents on laurel camphor, *l*-borneol being formed at the same time (Berthelot, Ann. Chim. Phys. [3] 56, 78; Montgolfier, *ibid.* [5] 14, 21), and in small proportions, with *l*-borneol, it is found among the products of the distillation of amber with potash (Berthelot and Buignet, Annalen, 115, 245).

Borneol is harder and less volatile than laurel camphor, and does not sublime in the bottles in which it is kept. It has a peppery camphoraceous odour and burning taste. M.p. 206°–207° (Plowman, Pharm. J. [3] 4, 709); b.p. 212° (Pelouze); sp.gr. 1·011 (Pl.). It is very slightly soluble in water, but dissolves readily in alcohol and ether. Removal of a molecule of water by phosphoric anhydride leaves the solid terpene *camphene* $C_{10}H_{16}$ (Wallach, Annalen, 230, 239). Concentrated hydrochloric acid (Berthelot, *ibid.* 112, 366) or phosphorus pentachloride (Kachler, Annalen, 197, 99) reacts with formation of *bornyl chloride* $C_{10}H_{17}\cdot Cl$. *Bornyl acetate* $C_{10}H_{17}\cdot OAc$ is a constituent of valerian oil (Bruylants), and may be produced by the action of acetic anhydride on borneol (Montgolfier, Ann. Chim. Phys. [5] 14, 50), and in a similar manner *bornyl benzoate* $C_{10}H_{17}\cdot OBz$ is obtained (Berthelot). Sodium reacts on borneol in solution in benzene with the formation of a crystalline *sodium salt*, $C_{10}H_{17}\cdot ONa$ (Kachler and Spitzer, Monatsh. 2, 235). The *methyl ether* $C_{10}H_{17}\cdot OMe$ is formed by acting on the sodium salt with methyl iodide (Baubigny, Zeitsch. f. Chem. 1868, 299). Nitric acid oxidises borneol with formation of dextrorotatory *camphor* $C_{10}H_{16}O$, in the first instance, and the reaction proceeding further *camphoric acid* $C_{10}H_{16}O_4$ and other products result (Laurent, Annalen, 22, 135; Pelouze, *ibid.* 40, 328; Kachler, *ibid.* 193, 143).

l-Borneol is a constituent of the following

oils: Valerian, *Valeriana officinalis* (Linn.) (Gerhardt, Annalen, 45, 34; Bruylants, Ber. 11, 455; Flück. a. Hanb. 379; Haller, Compt. rend. 103, 151); Canada snake root, *Asarum canadense* (Power and Lees, Chem. Soc. Trans. 81, 63); *Abies canadensis* (Linn.) and *Abies pectinata* (D.C.) (Bertram and Walbaum, Ber. 26, 685); Siberian fir, *Abies Sibirica* (Schindelmeiser, J. Russ. Phys. Chem. Soc. 34, 954; Golubeff, *ibid.* 36, 1096). It is also contained in the fusel oil of the crude spirit obtained by the fermentation of the sugar of madder, and formerly known as *madder camphor* (Jeanjean, Annalen, 101, 95); and is also contained in Ngai camphor, the name given to the solid part of the essential oil of *Blumea balsamifera* (D.C.). (Hanbury and Plowmann, Pharm. J. [3] 4, 709; Flückiger, *ibid.* [3] 4, 828; Schimmel's Report, April, 1910, 148). On oxidation with nitric acid, *l*-borneol yields lævorotatory camphor.

Inactive borneol, the racemic mixture of *d*- and *l*-borneol, has been obtained by the distillation of the crude product of the action of sulphuric acid on turpentine (Armstrong and Tilden, Chem. Soc. Trans. 35, 752); an ester of *i*-borneol is also obtained by treating pinene with oxalic acid (Schindelmeiser).

*Iso*borneol, a structural isomeride of borneol, and an intermediate product in the manufacture of synthetic camphor, was first obtained by Bertram and Walbaum (J. pr. Chem. [2] 49, 1) from camphene, a solid terpene $C_{10}H_{16}$, obtained by the action of sodium acetate and glacial acetic acid on pinene hydrochloride at 200°. Camphene is warmed with a mixture of acetic acid and a little sulphuric acid and the resulting acetate is decomposed by alcoholic potash. It is now prepared from pinene hydrochloride directly by the action of boiling glacial acetic acid in the presence of a small quantity of a metallic salt such as anhydrous zinc chloride (Weizmann and Clayton Aniline Co. D. R. P. 207155). It differs from borneol by its greater volatility, its higher melting-point (212°), and its greater solubility in benzene and light petroleum (*v.* OILS, ESSENTIAL).

Camphors isomeric or homologous with borneol. *Cineol* $C_{10}H_{18}O$ is the chief constituent of the volatile oils of santonica, *Artemisia maritima* (Linn.), var. *Stechmanniana* (Besser) (Kraut, J. 1862, 460; Kraut and Wahlforss, Annalen, 128, 293; Hell and Stürcke, Ber. 17, 1970; Wallach and Brass, Annalen, 225, 291), and of cajeput, *Melaleuca cajeputi* (Roxb.), *cajeputol* (Wallach, *ibid.* 225, 315). Cineol is also contained in the volatile oils of *Eucalyptus globulus* (Labill.) (Faust and Homeyer, Ber. 7, 1429; Jahns, *ibid.* 17, 2943) and of rosemary, *Rosmarinus officinalis* (Linn.) (Weber, Annalen, 238, 95), and many other essential oils. Artificially it may be obtained by the action of aqueous phosphoric acid on terpilenol, or in small proportions by treating terpinhydrate with mineral acids (Wallach, Annalen, 239, 18). It boils at 176° (Wallach), 172·5° (H. and S.). It does not alter a ray of polarised light. The terpenes *dipentene* $C_{10}H_{16}$ and *dicinene* $C_{20}H_{32}$ result from the action of phosphoric anhydride (H. and S.). Oxidised by permanganate, *cineolic acid* $C_{10}H_{18}O_5$ and other products are formed (Wallach and Gildemeister, Annalen, 246, 268). Cineol absorbs hydrochloric acid gas, forming the crystalline *hydrochloride* $C_{10}H_{18}O,HCl$ (Hell and Ritter, Ber. 17, 1977). A characteristic reaction for cineol is that, shaken with a saturated solution of iodine in potassium iodide, there is formed a glutinous mass of minute shining greenish crystals.

For the detection of cineol in essential oils, Herschsohn (Chem. Zentr. 1893, i. 503) shakes 3–15 drops of the oil with 10–50 milligrams of iodole (tetraiodopyrolline), adding more oil if necessary, to form a clear solution; he then allows the mixture to stand for 24 hours. If crystals separate, these are washed with light petroleum and subsequently boiled with aqueous potash, when the odour of cineol is developed.

The volatile oils of the following contain liquid isomerides of borneol: Buchu leaves, *Barosma betulina* (Bart. and Wendl.), *B. crenulata* (Hooker), *B. serratifolia* (Willd.), contain an oil $C_{10}H_{18}O$, boiling at 205°–210°, with *diosphenol*, a crystalline camphor (Flückiger, J. 1880, 1081), also obtained by Spica (Gazz. chim. ital. 15, 195) from *B. crenata* (Linn.). Diosphenol $C_{10}H_{16}O_2$ melts when pure at 83°–84°, boils at 109°–110° under 10 mm., and is optically inactive (Semmler and McKenzie, Ber. 38, 1158; *cf.* Kondakoff, J. pr. Chem. [2] 54, 433; Chem. Zeit. 1906, 1090; Kondakoff and Bachtschéeff, J. pr. Chem. [2] 63, 49). Citronella, *Andropogon Nardus* (Linn.) (Wright, Pharm. J. [3] 5, 233); Coriander, *Coriandrum sativum* (Linn.) (Kawalier, J. 1852, 624; Grosser, Ber. 14, 2485); Galangal, *Alpinia officinarum* (Hance) (Vogel, Berzelius Jahresb. 24, 479); Geranium, *Andropogon Iwarancusa* (Linn.), *A. Schœnanthus* (Linn.) (Jacobson, Annalen, 157, 232); *Pelargonium radula* (L'Héril) (Gintl. J. 1879, 941); Hops, *Humulus lupulus* (Linn.) (Wagner, J. 1853, 516; Personne, J. 1854, 654; Ossipoff, J. pr. Chem. [2] 28, 448); Lemon, *Citrus medica* (Linn.) (Tilden, Pharm. J. [3] 9, 654); Sage, *Salvia officinalis* (Linn.), *Salviol* (Muir, Chem. Soc. Trans. 37, 678); Tansy, *Tanacetum vulgare* (Linn.) (Bruylants, Ber. 11, 452); Angustura, *Cusparia febrifuga* (Humbol.), yields a volatile oil containing $C_{13}H_{24}O$, which is a higher homologue of Borneo camphor (Herzog, J. 1858, 444) (*v.* OILS, ESSENTIAL).

Common and allied camphors. *Laurel Camphor; Dextro Camphor.* (*Camphre*, Fr.; *Campher*, Ger.) $C_{10}H_{16}O$. Common camphor is contained in all parts of the camphor laurel, *Cinnamomum Camphora* (Nees and Eberm.), a tree inhabiting Japan, Formosa, and Central China, and cultivated for its foliage in the south of Europe and generally in warm climates. It occurs also as a constituent of the volatile oils of Lavender, *Lavandula vera* (De C.) (Dumas, Annalen, 6, 248; *cf.* Flück. a. Hanb. 478); Rosemary, *Rosmarinus officinalis* (Linn.) (Lallemand, *ibid.* 114, 197); Sage, *Salvia officinalis* (Linn.) (Muir, Chem. Soc. Trans. 37, 678); and Spike, *Lavandula spica* (De C.) (Lallemand).

Although camphor is at the present time manufactured artificially, most of the camphor of commerce is still obtained from the camphor laurel, the industry for many years being confined to the interior of China, the island of Formosa, and Japan; though recently experiments have been undertaken for the production of natural camphor in Florida, German East Africa, and Ceylon. In Formosa the camphor

industry before the China-Japanese war was nominally in the hands of the Chinese, but owing to the savage state of the interior of the island, and the unscrupulous methods of the dealers, it had declined to small and unimportant proportions. Afterwards Japan assumed the control of the industry, and it was made a government monopoly in 1899, and this was extended to Japanese camphor in 1903. Since the establishment of the monopoly the old crude methods of obtaining the camphor (Flück. a. Hanb. 513) have been replaced by more modern ones. The camphor wood in the form of chips is steamed in roughly built furnaces, and the camphor which is driven off is condensed in cooled wooden vessels, and freed from most of the oil by draining, crude or 'grade B' camphor being thus obtained. For the production of refined or 'grade A' camphor, the crude material is heated in large iron retorts, through which a current of air is passed. For the first 48 hours only sufficient heat is applied to drive off the water and oil. The retorts are then connected with a condensing chamber, the roof of which is cooled by running water, and are heated to a high temperature in order to volatilise the camphor. It is then formed into blocks in wooden moulds and pressed first with steam, and finally by a very high hydraulic pressure (Collins, J. Soc. Chem. Ind. 1904, 75). The yield of camphor is greater in winter than in summer, while the reverse is true of the oil. In summer, a charge of 120 kilos. of wood gives 2·4 kilos., or 2 p.c. of camphor, and 1·8 litres of oil; in winter, 3 kilos., or 2·4 p.c. of camphor and 0·5–0·7 litre of oil.

Crude camphor appears in commerce as a coarse wet powder of a greyish-white colour. Chinese crude camphor is packed in round wooden pots of about 150 lbs. net content; Japanese in lead-lined wooden boxes containing about 130 lbs. net. The principal impurities of crude camphor are water, camphor oil, iron, sand, wood, &c. *Light oil of camphor* has a sp.gr. of 0·895–0·920; b.p. 170°–180°, and contains pinene, camphene, dipentene, phellandrene, &c. *Heavy oil of camphor*, having a sp.gr. of 0·960–0·970, and b.p. 240°–300°, contains sesquiterpene, safrol, eugenol, cineone, fenchone, terpinone, &c. Besides these compounds, both of the oils contain a large amount of camphor in solution. Before refining crude camphor, the oil and water must be got rid of, as the oil gives the refined camphor a fatty touch, and the water renders it opaque. The elimination of water and oil is often effected by washing in a centrifugal machine with small quantities of water; the liquid draining off contains both oil and water. The separation is also done by hydraulic pressure, or by crystallisation from boiling benzene or light petroleum. Resublimation in Europe is done principally in glass retorts, yielding a round concave cake weighing 6–8 lbs., having an opening in the centre. In America the camphor is sublimed from flat iron pans with iron covers, yielding plates of about 18 inches square and 1 inch thick, weighing from 8 to 10 lbs. The process consists in mixing the camphor with a little lime, charcoal, or iron filings, according to the quality, and charging each pan with about 12 lbs. of material; the subliming pans are heated slowly for 2 hours, and then fired rapidly up to 190°, this temperature being kept for from 12 to 16 hours. After cooling, the refined product is removed from the cover by slightly heating, and is then cut into the desired shape (Drobegg, J. Soc. Chem. Ind. 1907, 38).

Purified camphor consists of colourless translucent masses traversed by numerous cracks, or, when slowly condensed, of hexagonal crystals. It can be broken, but is too tough to admit of being powdered by trituration. This may, however, be readily effected if a little alcohol be added, which escapes again during the operation. Camphor is used in medicine for its stimulant and antiseptic properties, and it is largely consumed by the natives of India. Sp.gr 0·992 (10°); m.p. 175°; b.p. 204°. It sublimes to some extent at ordinary temperatures (*cf.* Folger, Y. B. Pharm. 1886, 232). Dextrorotation (Landolt, Annalen, 189, 334). Refraction coefficient (Kanonnikoff, J. pr. Chem. [2] 31, 348). Camphor, in common with chloral hydrate and some other substances, rotates in a peculiar manner on the surface of water (Tomlinson, Phil. Mag. [4] 46, 376; Pharm. J. 4, 654 and 672; Chem. News, 36, 215; 37, 72; 52, 50). Water dissolves it very sparingly, but it is readily soluble in alcohol, ether, or chloroform. Mixed with chloral hydrate, it forms an oily liquid, $C_{10}H_{16}O,CCl_3CHO,H_2O$, which has been employed in medicine (Brown, Pharm. J. [3] 4, 729; Saunders, *ibid.* [3] 7, 89; Cazeneuve and Imbert, Bull. Soc. chim. [2] 34, 209; Zeidler, J. 1878, 645; Albright, Amer. J. Pharm. 1886, 282). Similar combinations take place between camphor and chloral alcoholate (Zeidler), phenol (Flückiger, Pharm. Chem. 2, 450), menthol (Kyle, Amer. J. Pharm. 1885, 429), and thymol (Symes, Pharm. J. [3] 9, 598).

Phosphoric anhydride removes water from camphor, forming *cymene* $C_{10}H_{14}$, together with other hydrocarbons (Armstrong and Miller, Ber. 16, 2259). With phosphorus pentachloride it yields *camphor dichloride* $C_{10}H_{16}Cl_2$. *Nitrocamphor* $C_{10}H_{15}(NO_2)O$ is prepared by reduction of chloronitro-camphor (Cazeneuve, Bull. Soc. chim. 47, 920; 49, 92; Schiff, Ber. 13, 1403), and this by treatment with sodium amalgam is converted into *amino-camphor* $C_{10}H_{15}(NH_2)O$ (Schiff). Of the bromine derivatives, *monobromo-camphor* $C_{10}H_{15}BrO$ is employed in medicine, and is an article of trade. It is prepared by treating camphor with bromine at 130°, and crystallising the mass obtained from light petroleum. It may be purified by recrystallisation (Maisch, Amer. J. Pharm. 44, 177; Gault, l'Union Pharm. 15, 266, Keller, J. 1880, 726). From alcohol it crystallises in colourless prisms or needles, from light petroleum either in long flat prisms or glossy scales. Monobromo-camphor has a weak camphoraceous odour and taste; m.p. 76°; b.p. 274° (Perkin, Annalen, Spl. 4, 125). It is insoluble in water, but soluble in alcohol, ether, chloroform, benzene, the fixed oils, and sulphuric acid. By the action of reducing agents, camphor is converted into *borneol*. This may be accomplished conveniently by adding sodium to an alcoholic solution of camphor (Jackson and Menke, Amer. Chem. J. 5, 271; Jackson, *ibid.* 6, 406). Hot alkaline permanganate (Grosser, Ber. 14, 2507) or nitric acid (Kachler, Annalen, 162, 262; 193, 143) oxidises camphor with the formation of *camphoric acid* $C_8H_{14}(COOH)_2$.

Synthetic Camphor; Inactive Camphor. Camphor manufactured from turpentine oil is now being brought into the market, and is competing with natural camphor. It is termed 'synthetic camphor' to distinguish it from the so-called 'artificial camphor,' which consists of pinene hydrochloride, and is unsuitable for the chief purposes to which camphor is applied. Synthetic camphor is identical with natural camphor, except that it is optically inactive. The first commercial process of obtaining camphor from oil of turpentine consisted essentially in converting the latter into pinene hydrochloride, which compound by elimination of hydrogen chloride yields camphene. Camphene is then converted into *iso*borneol, which, like natural borneol, yields camphor on oxidation. For the preparation of pinene hydrochloride, oil of turpentine, which contains about 70 p.c. of pinene, is treated with dry hydrogen chloride, whereby solid pinene hydrochloride is obtained, together with a liquid hydrochloride which is not suitable for the manufacture of camphene. This liquid hydrochloride contains a considerable proportion of the solid hydrochloride in solution, which may be recovered by oxidising the oily product with dilute nitric acid, or by treatment with concentrated or fuming sulphuric acid, which causes polymerisation of the liquid hydrochloride (Eng. Pat. 7319, 1908). The preparation of camphene by the removal of hydrogen chloride from pinene hydrochloride (Wallach, Annalen, 239, 6; Brühl, Ber. 25, 147; Reychler, Bull. Soc. chim. [3] 15, 371) was at first attended with difficulty; the yield was small, and the product was liable to contain chloride. During the last ten years the following methods have been patented for the production of camphene in large quantities, many of which are claimed to give almost theoretical yields and a product free from chloride: Heating the hydrochloride with bases of the aliphatic series, such as methylamine, or with piperazine or piperidine (U.S. Pat. 707270, 1902); by heating the hydrochloride with alcoholic, aqueous, or gaseous ammonia (U.S. Pat. 707271, 1902); by heating with aqueous sodium hydroxide or ammonia in presence of a soap (U.S. Pat. 725890, 1903); by heating with lead acetate in glacial acid solution (Fr. Pat. 349896, 1904); by heating with a metal and an oxidising agent, such as zinc and barium peroxide in molecular proportions (Fr. Pat. 361333, 1905); by heating with alkali phenolate either anhydrous or in presence of water (Eng. Pat. 16429, 1906); by heating with lime or other similar oxide (Fr. Pat. 375364, 1907; 384955, 1907); by heating with alkali, and alkali or alkaline earth salt of sulphonic acid of the benzene or naphthalene series (Eng. Pat. 10783, 1907); by heating with *α*- or *β*-naphthylamine (D. R. P. 206386, 1907), or with aniline (D. R. P. 205850, 1907); by heating with a meta- or pyro-borate, silicate, phosphate, or arsenate in aqueous solution (D. R. P. 205295, 1908); by heating with phenol, cresol, or naphthol, and the carbonate of an alkali or alkaline earth metal (Eng. Pat. 13902, 1909). The camphene can usually be separated by steam distillation. Bertram and Walbaum (J. pr. Chem. [2] 49, 1) made the discovery that camphene is converted into *iso*borneol by warming with a mixture of acetic acid and a little sulphuric acid, and decomposing the resulting *iso*bornyl acetate by alcoholic potash. This method is employed on the manufacturing scale. Camphene has also been directly converted into *iso*borneol by boiling in acetone solution with half its weight of 20 p.c. H_2SO_4 for 10 hours, or in an autoclave at 100° for a shorter time (Fr. Pat. 385341, 1907). The *iso*borneol purified by crystallisation from light petroleum or benzene is then oxidised to camphor. For this purpose various oxidising agents are employed, many of which have been patented. Amongst these are: potassium permanganate in glacial acetic acid (Ber. 33, 3430); aqueous solution of permanganate, employed with a benzene solution of *iso*borneol (Fr. Pat. 341513, 1904); potassium permanganate in acetone solution (D. R. P. 38311, note); chlorine, either gaseous or in solution (Eng. Pat. 28035, 1904); chromic acid or chromates at a temperature of 90° (Eng. Pat. 26779, 1904); nitric acid in which the presence of 'nitrous oxide' is essential (Eng. Pat. 9857, 1907); oxygen, oxides of heavy metals or peroxides (Fr. Pat. 385352, 1907). According to U.S. Pat. 790601, 1905, *iso*bornyl acetate and other isobornyl esters can be directly oxidised to camphor without previous saponification.

Camphene can also be directly oxidised to camphor (Armstrong and Tilden, Ber. 12, 1756), and the following processes have been patented: Treatment with ozone at a temperature of 80° (Eng. Pat. 21294, 1890); treatment with hot air or oxygen (Eng. Pat. 3555, 1896); oxidation by potassium permanganate in acetone solution (addition to Fr. Pat. 349896, 1904); treatment of camphene at 180° with an oxidising agent such as chromic acid converts it into oxonide, $C_{10}H_{16}O_3$, which loses oxygen on treatment with water, and is converted into a lactone, camphenolide, which yields camphor on heating in presence of water (Fr. Pat. 361333, 1905); oxidation with a per- salt of potassium and sulphuric acid (Fr. Pat. 389092, 1908).

Another method of obtaining synthetic camphor depends on the formation of bornyl esters by the direct action of various organic acids on turpentine oil. The working of the following process was undertaken, in 1902, by the Ampère Electro-Chemical Co.; anhydrous turpentine was heated at 120°–130° with anhydrous oxalic acid, and the resulting product, supposed to consist of a mixture of borneol, camphor, bornyl oxalate, and formate, with waste polymerisation products, was saponified with lime and distilled with steam. The resultant camphor and borneol were separated and oxidised to convert the borneol into camphor. The assumption of the direct formation of camphor by the action of oxalic acid on pinene has since been proved to be erroneous. A large amount of by-products are obtained, while the amount of borneol or *iso*borneol formed is not sufficient to ensure the commercial success of the process, which seems to have been abandoned (Pond, J. Soc. Chem. Ind. 1907, 385). Similar methods, based on the direct formation of bornyl esters from pinene hydrochloride, have been patented: a solution of pinene hydrochloride and an alkali formate or oxalate in alcohol and water is heated for 10 hours to 120° (Eng. Pat. 5549, 1904); pinene hydrochloride

in acetic acid solution is heated with lead acetate (Fr. Pat. 349896, 1904); acetate, stearate, or phenate of sodium, potassium, calcium, or other metals, with an excess of either acetic acid, stearic acid, or phenol, in presence of a dehydrant, are shaken with the solid pinene hydrochloride (Fr. Pat. 382790, 1906); by heating pinene hydrohalogenides with fatty acids and a halogen compound of zinc in presence of cobaltous chloride or other suitable inorganic salt (Eng. Pat. 22129, 1907).

(For analyses and points of difference between natural and commercial synthetic camphor, *see* Crane and Joyce (J. Soc. Chem. Ind. 1907, 386), and Lohmann (Ber. deut. Pharm. Ges. 19, 222).)

Lævo camphor; *Matricaria camphor.* This camphor occurs naturally in the volatile oil of Feverfew, *Pyrethrum Parthenium* (Sm.) (Chautard, Compt. rend. 37, 166); and in the oil obtained from the fresh twigs and leaves of *Artemisia nana* (Pursh.) (Whittelsey, Chem. Zentr. 1909, ii. 2160). It can be prepared by oxidation of camphene obtained from lævorotatory pinene (Riban, Bull. Soc. chim. 24, 19), and by oxidation of *l*-borneol with nitric acid (Pope and Harvey, Chem. Soc. Trans. 79, 76). It differs from common camphor only in its behaviour towards polarised light.

The following are the most important volatile oils which contain isomerides of camphor: *Arbor vitæ*, *Thuya occidentalis* (Linn.), *Thujol* (Jahns, Arch. Pharm. 221 748); Chamomile *Anthemis nobilis* (Linn.), *Anthemol* (Köbig, Annalen, 195, 95); Cowbane, *Cicuta virosa* (Linn.) (Trapp, J. 1858, 444); Galbanum, one of the products of the distillation of galbanum resin (Kachler, Ber. 4, 39; Mössmer, Annalen, 119, 257); German Chamomile, *Matricaria chamomilla* (Linn.) (Kachler, Ber. 4, 36; Bizio, J. 1861, 681); Hyssop, *Hyssopus officinalis* (Linn.) (Schmidt, Lehrb. Ph. Ch. 2, 830); Elecampane, *Inula Helenium* (Linn.), *Inula*, or *Alant camphor*, a liquid with the odour of peppermint, which, when treated with phosphoric anhydride, yields cymene, and with chromic acid, terephthalic acid (Kallen, Ber. 9, 154); Nutmeg, *Myristica fragrans* (Houtt.), *Myristicol* (Wright, Ber. 6, 147); Pennyroyal, *Mentha Pulegium* (Linn.) (Kane, Annalen, 32, 286; Butleroff. J. 1854, 594); Pichurim Beans, *Nectandra Puchury* (Nees), (Müller, J. 1853, 514); Sage, *Salvia officinalis* (Linn.), m.p. 174°; b.p. 205° (Muir, Chem. Soc. Trans. 37, 678); and Wormwood, *Artemisia Absinthium* (Linn.), *Absinthol* (Beilstein and Kupffer, Annalen, 170, 290).

The more important homologues of common camphor are:

Matico camphor $C_{12}H_{20}O$, contained in the volatile oil of matico leaves, *Piper angustifolium* (Ruiz and Pavon), which on standing deposits the camphor in crystals; m.p. 94°. Concentrated hydrochloric acid colours it intense violet, changing to blue and green (Kügler, Ber. 16, 2841).

Cedar camphor $C_{15}H_{26}O$, a crystalline mass obtained from the volatile oil of *Juniperus virginiana* (Linn.); m.p. 74°, b.p. 282°. Yields *cedrene* $C_{15}H_{24}$, when treated with phosphoric anhydride (Walter, Annalen, 39, 247; 48, 35).

Cubebs camphor $C_{15}H_{26}O$, a constituent of the volatile oil of the old fruits of the *Piper Cubeba* (Linn.). The crystals melt at 68·7°–70° (W.), 65° (S.), 67° (S. and W.); b.p. 148° (S.). Dehydrated by sulphuric acid, *cubebene* $C_{15}H_{24}$ is formed (Blanchet and Sell, Annalen, 6, 294; Winckler, *ibid.* 8, 203; Schmidt, Zeits. f. Chem. 1870, 190; Schaer and Wyss, J. 1875, 497).

Ledum camphor $C_{15}H_{26}O$ (?), obtained from the volatile oil of Marsh Tea, *Ledum palustre* (Linn.). Needles, m.p. 104°–105°; b.p. 292°. By the action of phosphoric anhydride, the *sesquiterpene* $C_{15}H_{24}$ is formed (Rizza, J. R. 19, 319; Trapp, Ber. 8, 542; Hjelt and Collan, *ibid.* 15, 2501; Hjelt, *ibid.* 28, 3087).

Patchouli camphor $C_{15}H_{26}O$ (?), a crystalline camphor contained in the volatile oil of *Pogostemon Heyneanus* (Benth.); m.p. 54°–59°; b.p. 206°. By the action of acetic anhydride it loses water and forms *patchoulene* $C_{15}H_{24}$ (Gal, Compt. rend. 1869, 68, 406; Montgolfier, Bull. Soc. chim. 28, 414; Maisch, Amer. J. Pharm. 1884, 84).

Sandalwood camphor, *Santalol*, a liquid camphor obtained from the volatile oil of *Santalum album* (Linn.); b.p. 310° (Chapoteaut, Bull. Soc. chim. 37, 303). Santalol, known commercially as gonorol, prepared from sandalwood by heating with a little alcoholic potash, contains, besides sesquiterpenes, an alcoholic constituent which can be separated into α-santalol and β-santalol. α-Santalol $C_{15}H_{23}OH$ forms the chief constituent of the oil. It is a thick, colourless liquid with a faint odour of sandalwood, b.p. 301°–302°, feebly dextrorotatory. β-Santalol is isomeric with α-santalol and is lævorotatory (Soden and Müller, Chem. Zentr. 1899, i. 1082; Soden, Arch. Pharm. 238, 353).

Thyme and allied camphors. *Thymol* $C_{10}H_{14}O$, *i.e.* $C_6H_3 \cdot Me \cdot (OH) \cdot Pr$. [1 : 3 : 4].

Thymol is a constituent of the volatile oils of Ajowan, *Carum copticum* (Benth. and Bork.) (Haines, Chem. Soc. Mem. 8, 289; Stenhouse, Annalen, 98, 269 and 307; Müller, Ber. 2, 130); Garden Thyme, *Thymus vulgaris* (Linn.) (Doveri, Annalen, 64, 374; Lallemand, Ann. Chim. Phys. [3] 49, 148); Horse Mint, *Monarda punctata* (Linn.) (Arppe, Annalen, 58, 41), and together with carvacrol in Wild Thyme, *Thymus Serpyllum* (Linn.) (Jahns, Ber. 15, 819; Febre, J. 1881, 1028). To extract it, the oils are shaken with a solution of caustic soda, when the thymol passes into the aqueous portion in the form of a soluble sodium salt, and is thus separated from the hydrocarbons. The alkaline solution is acidified with hydrochloric acid, which precipitates the crude camphor. It may then be purified by crystallisation from glacial acetic acid or alcohol. Another plan is to submit the oils to fractional distillation and to precipitate the thymol from the heavier portions of the distillate by the application of cold (*v.* OILS, ESSENTIAL).

Thymol has the odour of thyme and a warm pungent taste; m.p. 50°; b.p. 222° (Stenhouse), 230° (Lallemand). It is sparingly soluble in water, but very soluble in alcohol, ether, and alkaline solutions. It forms a liquid with menthol (Kyle, Amer. J. Pharm. 1885, 429), camphor (Symes, Pharm. J. [3] 9, 598), berberine (Lloyd, New Remedies, 1881, 195), but not with chloral hydrate (Symes; *cf.* Mazzara, Gazz. chim. ital. 13, 272). If a solution containing thymol be warmed with half its volume of glacial acetic acid together with more than its volume of sulphuric acid, a deep red-violet colour is developed. This reaction is obtained even in very dilute solutions (Robbert, J. Th. 1881, 109; Wolff, Zeitsch.

anal. Chem. 22, 96). (For other test reactions, *see* Störmer (Arch. Pharm. [3] 25, 36; Pharm. Zeit. 31, 744; Hirschsohn, Pharm. J. [3] 12, 21). For colour reactions with sugars, *v.* Lindo (Chem. News, 55, 239).)

Phosphoric anhydride splits the thymol molecule into *propylene* C_3H_6 and *m- cresol* $C_6H_4Me{\cdot}OH[1:3]$. Phosphorus pentasulphide deoxidises it with the formation of *p- cymene* $C_6H_4{\cdot}Pr{\cdot}Me[1:4]$ (Fittica, Annalen, 172, 305). Well-defined *salts* are formed with *sodium* $C_{10}H_{13}{\cdot}ONa$, *mercury* $C_{10}H_{13}{\cdot}HgOH$, and *aluminium* $(C_{10}H_{13}O)_3Al$. By the action of nitrous acid on thymol, *isonitrosothymol* $C_{10}H_{12}(N{\cdot}OH)O$ is obtained in yellow needles (Schiff, Ber. 8, 1500), and from this compound *nitrothymol*

$$C_{10}H_{12}(NO_2)O$$

(Schiff) and *aminothymol* $C_{10}H_{13}(NH_2)O$ are derived. *Methyl ether* $C_{10}H_{13}OMe$ (Engelhardt and Latschinoff, Zeitsch. f. Chem. 1869, 43); *Ethyl ether* $C_{10}H_{13}{\cdot}OEt$ (Jungfleisch, Zeitsch. f. Chem. 1865, 532); *Acetate* $C_{10}H_{13}{\cdot}OAc$ (Paternò, Bull. Soc. chim. 25, 32); *Benzoate*, $C_{10}H_{13}{\cdot}OBz$ (E. and Z.); *Carbonate* $(C_{10}H_{13}O)_2CO$ (Richter, J. pr. Chem. [2] 27, 505); *Phosphates* $(C_{10}H_{13}O)_3PO$ (E. and L.). $(C_{10}H_{13}O)_2HO_2PO$ (Kreysler, Ber. 18, 1705; Discalzo, Gazz. chim. ital. 15, 280), and

$$(C_{10}H_{13}O)(HO)_2PO$$

(D., *loc. cit.*).

For estimation of thymol in essential oils, Kremers and Schreiner (Chem. Zentr. 1897, ii. 147) recommend the following process: A known weight of the sample is mixed in a glass-stoppered burette with an equal volume of light petroleum and agitated with 5 p.c. aqueous potash till no further diminution of the oily layer takes place, and a drop of the oil dissolved in 20 drops of chloroform, on gently warming with a small piece of sodium hydroxide, does not turn red. The alkaline liquid can be titrated with iodine, but it appears the results obtained by titration are about 3 p.c. lower than the decrease in volume. (For iodometric estimation, *see also* Messinger (J. pr. Chem. [2] 61, 247).)

Thymol is used in medicine as an antiseptic.

Camphors isomeric with thyme camphor. Carvol $C_{10}H_{13}{\cdot}OH$ is a liquid isomeride contained in the following volatile oils: Caraway-seed, *Carum carvi* (L.) (Völckel, Annalen, 85, 246); Dill-fruit, *Peucedanum graveolens* (Hiern) (Nietzki, N. Handb. Chem. 2, 986); Spearmint, *Mentha viridis* (Linn.) (Gladstone, J. 1863, 548), and Crisped Mint, *Mentha aquatica* (Linn.) (Schmidt, Lehrb. Ph. Chem. 2, 845). Carvol is distinguished from other constituents of volatile oils by its power of combining directly with sulphuretted hydrogen to form the crystalline *hydrosulphide* $(C_{10}H_{14}O)_2H_2S$ (*cf.* Flückiger, Ber. 9, 468). *Carvacrol, cymophenol* $(C_6H_3{\cdot}Me{\cdot}(OH),Pr)[1:2:4]$ is a thick oil closely related chemically to thymol. It is formed by distilling carvol in presence of solid phosphoric acid or caustic potash, and occurs in the following volatile oils: *Origanum hirtum* (Linn.) (Jahns, J. 1879, 942). *Satureia hortensis* (Linn.) (Jahns, Ber. 15, 816); *S. montana* (Linn.) (Haller, Bull. Soc. chim. 37, 411); and *Thymus Serpyllum* (Linn.) (Jahns,) (*v.* also Terpenes). A. S.

Iso-**CAMPHOR** *v.* Ketones.

CAMPOBELLO YELLOW *v.* Naphthalene colouring matters.

CANADA BALSAM *v.* Balsams; and Oleo-resins.

CANADA PITCH or **HEMLOCK SPRUCE RESIN** *v.* Resins.

CANADOL. Petroleum ether or ligroïn. That portion of refined petroleum which boils at about 60° and has sp.gr. of 0·65 to 0·70 consists mainly of normal hexane (*v.* Paraffin; and Petroleum).

CANANGA OIL *v.* Oils, Essential.

CANARIN. A yellow colouring matter obtained by the action of bromine or a mixture of potassium chlorate and hydrochloric acid or ammonium persulphate upon potassium or ammonium thiocyanate; it probably consists of $C_8H_6ON_2S_7$ (Goldberg, J. pr. Chem. 1901, ii. 63, 465; 64, 439; *cf.* H. Schmid, Dingl. poly. J. 251, 41). (For details of mode of preparation, *v. ibid.* 253, 130; also J. Soc. Chem. Ind. 3, 476.) Cloth dyed with canarin resists light and soap. Neither concentrated acids nor alkalis destroy it or dissolve it out of the fibre. Bleaching powder has no action upon it. Acts as a mordant for basic aniline dyes.

CANDELILLA WAX. A wax obtained from Candelilla or Mexican wax plant, growing in a number of Mexican states. Hard, opaque, and colourless solid; sp.gr. 0·9825; m.p. 67°–68°. Soluble in chloroform and carbon disulphide. Appears to consist largely of pentriacontane $C_{35}H_{72}$ (*see* Waxes).

CANDLES. Candles represent some of the most ancient and most useful forms of illuminants. The excellence of a candle depends on the nature of the wick and of the combustible matter, and on the manner and extent in which these are apportioned. The prototype of the candle was undoubtedly the torch, which must be regarded as a huge wick with the minimum amount of combustible matter, this proportion being gradually altered until the ratio used at present, viz. about 1 part wick to 50 parts of combustible matter, is reached.

The following table shows the stages in the development of candles.

Torch. Pine branches or slips (Lat. *tæda*), saturated, naturally or artificially, with resinous or fatty matter.

Link. Rope-strands steeped in rosin, tar, or pitch; in olden times, doubtless, in asphalt or bitumen.

Flambeau. A core of hemp, soaked in rosin and coated with crude beeswax. Later, the outer coat was made of bleached wax.

Dips. Wicks of rush-pith (rush-lights), crude flax or cotton, and subsequently of twisted cotton yarn, coated with beeswax or tallow by repeated dippings.

Moulds. (Introduced about the 15th century by the Sieur de Brez.) Hard tallow, spermaceti, stearine, or paraffin wax, cast round the wick in a mould.

In addition to these varieties may be mentioned *rolled*, *poured*, and *drawn* candles.

Dips, the cheapest, as well as the oldest form of candle, were made until comparatively lately of tallow or household grease. Beeswax candles were mostly poured, drawn, or rolled. The great advantage of the 'dip' lies in the ease with which it can be made. The thrifty housekeeper was wont to set aside the superfluous

kitchen fat for melting day, when part went to make soap, whilst the harder portions were formed into candles. The fat was thrown into boiling water and boiled three or four times with a little salt to 'render' it. The dirt and impurities being removed by subsidence, the clean liquid fat was run through a strainer into the candle pan. Some skill and experience were required to regulate the temperature of the melted fat. If too hot, the liquid fat would run off the wicks; if too cold, the material would congeal too quickly and adhere to the wicks irregularly and in lumps. In households these would be rushes, divested of their peel with the exception of a thin strip which was left to give strength to the pith. These were usually tied in bunches of four, so that one wick could be held between each pair of fingers, and thus be immersed in the liquid fat. A short time was allowed after each dipping to cool the last coat. Four dippings mostly sufficed, when the finished candles were hung up in an airy loft to harden and whiten.

In dips as manufactured on a large scale, the wicks are of twisted cotton, and are strung on rods, each rod holding eight. The workman, holding an end of the rod in either hand, first immerses the wicks in very hot tallow, in order that their fibres may be thoroughly saturated, and then, as each rod is ready, it is slid on to a cross frame to cool; the wicks are then redipped in tallow at a temperature little above its solidifying point, till the desired weight is obtained. As a rule four 'dippings' are required.

Many devices exist for reducing labour and ensuring uniformity of result in manufacturing dips. Of these contrivances, the 'Edinburgh wheel' is the best known. It consists of a long pole, pivoted vertically, and having mortises cut about its centre through which pass long wooden bars, each pivoted at its centre on an iron pin. These bars carry frames at their extremities, each of which, in their turn, holds about eight wick-rods. The post revolves, and as each bar with its frame passes over the melting pan, it is pulled down, so as to immerse the wicks. The opposite frame restores equilibrium, and the rotating and dipping are proceeded with until the proper weight is obtained, which is signalled by some contrivance on the post, itself the object of much inventive ingenuity. The most perfect apparatus of this kind was patented by Price's Candle Company and worked at the Inventions Exhibition in London in 1885.

Rolled, poured, and drawn candles. Rolled candles are now almost obsolete. Formerly, the larger sizes of church candles were made by 'rolling' a cake of warm wax, kneaded until it was plastic, round a wick, and imparting the necessary smoothness and uniformity by means of a rolling-pin. This process has now been entirely superseded by that of 'pouring.' 'Drawing' is resorted to only in the case of cables of small sizes, and tapers.

In *pouring*, a similar apparatus to that used in dipping is employed, but instead of the wicks being dipped, the melted beeswax is poured over them whilst the frame is kept in rotation (Fig. 1). In the larger sizes, the wicks have to be reversed from time to time to ensure a uniform thickness. The workman ascertains the correct dimensions by measuring with a piece of tape. After every two or three pourings, according to the weather, the hoops are hung in a current of air to cool. When the candles are of the requisite thickness, they are severed from the frame and placed on a smooth marble slab. The operator then rolls them to and fro under a board, on which he leans with his full weight. By this process, which requires much skill and practice, the irregularities are smoothed away, and the candles, in the hands of a skilful workman, assume the evenness of outline of moulded candles, with a peculiar softness, indescribable, though unmistakable when once identified. The ends of the candles are now cut clean with a sharp knife, and their tips shaped with the finger and a small strip of wood.

FIG. 1.

Obviously this process, which involves much skilled labour, must render beeswax candles very expensive. They are, indeed, the most costly form of illuminant. Their use is confined to churches and, to a small extent, to carriage lamps, in which formerly no other candle could be employed, by reason of the strong spring, although now several efficient substitutes exist and are in use.

To understand the favour which beeswax continued to enjoy long after the introduction of stearine and paraffin wax candles, which are not only much cheaper, but give a better light, we must take several circumstances into account. The first and, doubtless, the most cogent fact lies in the sharp contrast which formerly obtained between beeswax and tallow, a contrast which finds mention in many a tale of social life, even as far back as the times of Haroun Alraschid. The candle at one period was absolutely the only means of illumination available, and formed a very considerable item in the household expenses. As only the rich could afford this luxury, the beeswax candle became intimately associated with the other signs of wealth, as essential, indeed, as arms or silver plate. The introduction of spermaceti, in the middle of the 18th century, greatly affected the use of beeswax, and this was quickly followed by the adoption of gas in houses. Within the last decades, the electric light has replaced both beeswax and spermaceti candles in houses where for centuries no other light was known.

To adapt the beeswax as it comes from the hive to the requirements of the chandler, but little is needed beyond the ordinary cleansing processes. The clean beeswax is run from the 'copper' over a rapidly rotating drum into cold

water, by which means it becomes divided into fine shavings. These are exposed to the influences of sun and air for several weeks, with occasional re-meltings and pourings, after which the now cream-white wax is ready for use.

Drawn candles are made by *drawing* a considerable length of wick through a pan of beeswax (Fig. 2), maintained at a regulated temperature by (fire or) steam. The wick is wound from one drum on to another. As it leaves the pan, it traverses a plate perforated with holes increasing from one sixteenth of an inch to half an inch in diameter, whereby the superfluous wax is stripped off, the coated wick as it emerges being of the diameter of the hole. When the wick is all wound off, the drums are reversed, the end of the coated cotton passed through the

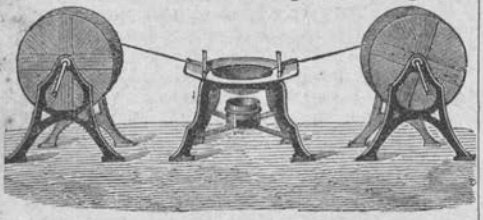


FIG. 2.

hole next in size, and the operation continued till the requisite thickness is obtained. This is seldom over half an inch, as the risk of cracking increases considerably with the diameter of the cable. In fact, this process is resorted to mainly for manufacturing 'spills' or lighting-wicks and the little tapers used for decorating Christmas-trees, but here also stearine in the former and paraffin wax in the latter have gradually displaced beeswax.

Mould Candles.—The chief variety of candles now made are mould candles. In order to ensure the proper burning of a candle, great attention must be bestowed upon the preparation of the wick, which is to the candle what the burner is to the gas. Till about 1820 the only wicks used were made of twisted cotton yarn, still to be seen in tallow dips. No means for consuming the wick being employed, snuffers had to be used to remove the charred and glowing end. Several expedients were devised to bring the wick automatically into contact with the air, and thus cause it to be consumed as the candle burnt. The best of these consisted in twisting the wick round a rod, and while in a state of tension, coating one side with size or other stiffening. This imparted a tendency to turn outwards and curl over, which to a great extent obviated the use of snuffers. Palmer, in 1852, invented a simple means for achieving the same result more thoroughly by introducing a fine thread coated with metallic bismuth into the substance of the wick, which thread he called the 'doctor.' When ignited, the easily fusible metal formed a globule on the end of the cotton, which by its weight bent the wick out of the flame into the air, when the oxygen could combine with the incandescent carbon, whilst the bismuth was volatilised. So successful was this device, that Palmer's 'metallic wick' candles achieved great popularity, especially for burning in candle lamps, for which large candles, sometimes weighing two pounds, were employed. The same device was again patented in Germany, by Varenkamp, as late as 1899.

But the introduction of 'braided' or 'plaited' wicks by Cambacères (in 1825) rendered such precautions unnecessary, the flat form of the wick, as now made, imparting a sufficient tendency to curve and bend outside the flame, where the cotton can burn completely. Now all except tallow dip candles are provided with these cores.

Before the wick can be used by the candle maker, it has to be 'pickled,' *i.e.* soaked in a solution of certain chemicals, which vary with the nature and purpose of the cotton. The preparation of these solutions forms one of the chief items in the manufacture of a good candle, and to carry it out thoroughly demands considerable practical experience; for the wick itself varies much in its composition, especially as regards the percentage of mineral matter. The plait, too, will vary in tightness, however carefully woven. Then again, a paraffin candle requires a thin wick to check a too-rapid supply of the liquid fuel. A beeswax or sperm candle, on the other hand, where the melted material is less mobile, or has less tendency to smoke, needs a thicker wick. The nature of the combustible, its melting-point, viscosity, and burning powers; the compounding of a suitable material by mixing candle materials from several sources; the selection of a wick that in number of threads, structure, and substance is adapted to the special material chosen; the subsequent treatment of this with such salts as will correct or enhance its tendencies;—these are some of the points which must be considered before proceeding with the more mechanical operations involved in candle making.

The wicks, which arrive at the factory from the cotton spinner in hanks, are placed two or three days before being wanted in the appropriate pickling solution. The object of 'pickling' the wick is to counteract either 'ashing' or 'smoking,' two great defects to which the candle is liable. The 'pickling' retards the too rapid combustion of the cotton, and vitrifies it slightly, so that when the wick protrudes from the flame any ash can drop off readily. In order to ensure the ready lighting of a candle, it has been proposed (Haase, Fr. Pat. 342527) to impregnate the protruding end of the wick with a solution of celluloid in acetone. Borax, nitre, sal ammoniac, potassium chloride or chlorate, and ammonium phosphate, are the principal salts employed for pickling; though almost every manufacturer has his own recipe. The proportion of the salt to water is usually about 2 oz. to 1 quart. The wicks are steeped in the solution for about 24 hours, after which they are placed on a perforated shelf, to allow the bulk of the liquid to drain off, and then transferred to a centrifugal machine rotating at a speed of nearly 1000 revolutions a minute, where the residual water is expelled without the slightest torsion or other disturbance in the structure of the threads, which would be almost inevitable in any other process. The hanks, still slightly damp, are placed in a cupboard heated by steam, and finally hung up in an airy room until required. The amount of salt remaining in the fibre must, of course, be very small, but it is quite sufficient to influence

materially the burning of the candle. The wick is next transferred to the spools, from which it passes to the moulding machine. This task is performed by boys, who wind the wick off the hank previously stretched on a circular rotating frame, on to 'spools' or bobbins on spindles (Fig. 3). As they wind, they let the wick run through their fingers, to detect any knots or other irregularities, which might interfere with the burning of the candle. The spools are now ready for transport to the machine, invented by Cahouet in 1850. The old 'hand-frame,' the forerunner and prototype of the present complicated apparatus, consists of a cluster of pewter moulds, introduced in 1724 by Freitag, held together by wooden collars at either end. Each mould is traversed longitudinally by a wick, which is secured by a peg at the top and wire at the base, and it has to be provided with a little loop of cotton, through which a wire is passed.

The butt ends of the moulds open into a trough about 1 inch

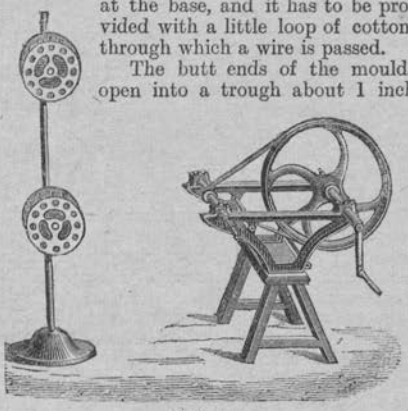


Fig. 3.

deep. Into this the hot material is poured until it is quite filled, and the whole frame is then placed in a tank of water, the temperature of which varies with the quality of candle, as will be explained presently. When quite cold, the candles are removed from the pipes by simply inverting the frame, the cake of superfluous candle material having been previously scraped off, and the wires and pegs withdrawn. As the pipes are made slightly conical and as the substance shrinks in cooling, there is seldom any difficulty in emptying the frame; if one or two of the candles should refuse to leave the moulds, a slight tap with a mallet speedily loosens them. This method is obviously slow and cumbrous, and were it not that some buyers will have hand-made goods, also that a few odd sizes for which it would not be worth while to keep special machines can only be made in hand-frames, these frames would have been abandoned long since. A hand-frame can be filled and emptied once an hour, whilst a modern machine will do thrice the amount of work in the same time.

Fig. 4 represents a candle machine of modern manufacture, for making candles with ordinary, *i.e.* not self-fitting, ends. It embodies the combined inventions and improvements made successively by Sampson (Eng. Pat. 2108, 1796); Binns (Eng. Pat. 2488, 1801); Morgan (Eng. Pat. 6610, 1834); Tuck (Eng. Pat. 7409, 1837); Palmer (Eng. Pat. 12077, 1848); Cowper (Eng. Pat. 1988, 1856); Humiston (Eng. Pat., in the name of Newton, 2541, 1857); Stainthorp (Eng. Pat., in the name of Pitman, 2556, 1857); Stainthorp (Eng. Pat. 740, 1860). The machine consists mainly, of a metal tank, G, in which the pipes are fixed with their butts opening in a trough and their tips emerging below. The tips are not of one piece with the moulds, but can slide up and down, fitting water-tight when drawn home. The motion is communicated by pistons, D, to which the tips are soldered, and which are perforated longitudinally.

The wicks wound on the above-mentioned spools, which rotate on a series of spindles at the base of the machine, pass up these perforations D. The tank G, which surrounds the pipes, is preferably connected with hot and cold water cisterns, or with cold water and steam. The moulds are made of pewter (an alloy of tin and lead), other materials, such as tin, brass, glass, &c., not having been found suitable in practice. Recently, porcelain moulds have been patented for paraffin candles (D. R. P. 195702), but it is very unlikely that they will be adopted

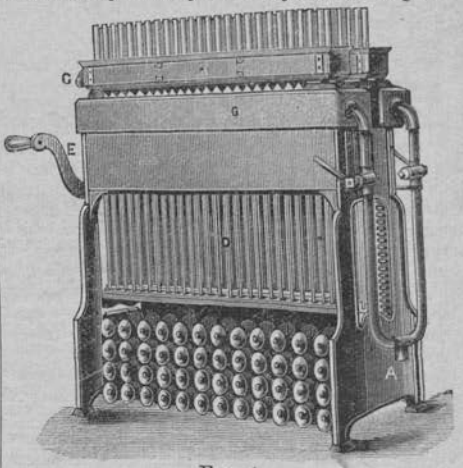


Fig. 4.

in candle works, as they are too costly; moreover, properly cleaned pewter moulds impart the same lustre to a candle that the porcelain mould gives. To commence the operation of casting, the wicks are drawn through the pistons, tips, and pipes, and temporarily secured in the troughs. These, and the moulds opening into them, are now filled roughly, merely to afford a starting-point for the wick, and emptied as soon as the material is cold. To effect this, the trough is scraped clear with a 'spud' (a blunt knife of the width of the trough), after which the handle E is slowly turned. This imparts, by means of rack-and-pinion gear, a vertical motion to the pistons, which mount up the pipes, carrying the dummy candles with them, and unwinding the wick from the spools. As the candles emerge from the pipes, they are received in a clamp frame C, which is held open by a spring handle. When the tips are clear of the trough, the clamp is closed, gripping the candles firmly. The handle is now turned the reverse way, causing the pistons to descend in the moulds till the tips close the ends securely.

Thus the wicks are left in the centre of the pipes, held by the dummies above and the spools below. The next step depends on the nature of the material used. If stearin candles are to be made, the tanks are charged with tepid water, the temperature of which the operator determines by his hand in preference to other methods. The reason for this precaution depends upon the highly crystalline structure of 'stearic' acid ('stearin'), which renders it liable to crack if chilled too suddenly, or to crystallise if cooled too slowly, whereby the appearance if not the structure of the candle would be impaired. Therefore the melted stearin is stirred, with the aid of simple machinery, while in the melting pans, till it assumes the consistency and appearance of gruel, in which state it is transferred to the 'jacks,' cans having a flat, wide spout, and thence to the moulds. When these are full, they are allowed to rest about 25 minutes until they are sufficiently hard to permit of their being withdrawn without fracture. The troughs are not scraped in this case, as the tops are hard enough if the candles are raised 2 inches. As soon as the pipes are filled again and the material set enough to hold the wick without extraneous aid, the upper row of candles, often while still warm, is removed into trays where they cool and bleach. This tendency of stearin to crack was a great obstacle to the success of these candles when they were first introduced. Among the various devices employed to overcome the defect was that of stirring a small proportion of arsenic into the melted stearin. This certainly broke the grain, but it was of course diffused into the air on burning the candles. When this became generally known, the prejudice against stearin candles was such as to affect injuriously the success of the new substitute for tallow, and to this day stearin candles enjoy but a comparatively limited popularity in this country.

Paraffin Candles. — At present, stearin candles are replaced in this country by candles made of a mixture of stearin and paraffin wax, except in the case of hollow candles (*see* below). In France, however, the stearin candle, being protected by customs duties on paraffin wax, holds its own against paraffin candles; and in that country, as also in Italy, stearin candles are manufactured in considerable quantities. In Germany and Austro-Hungary, the stearin candle is gradually being ousted by the paraffin candle. When, in 1854, James Young obtained from shale oil a pure white paraffin, which was subsequently made into candles under a patent of J. K. Field, the immediate popularity of the novel illuminant left little doubt as to what would be the material of the candle of the future. Even the most enthusiastic optimist of that day would have hesitated before accepting the prophecy that paraffin candles would be sold at half the price of tallow dips, as is the case to-day.

The main difficulty experienced in the early stages of the manufacture of paraffin candles, arose from want of precaution in regulating the temperature while casting. The same machine can be employed for either paraffin or stearin candles, but when paraffin wax is to be used, the water in the tanks is raised to a temperature of nearly 200°F., by passing steam through the pipe. Also the paraffin wax itself is heated to about 170°–180°F., and poured in a highly mobile state. When the pipes are filled, the hot water is discharged from the tanks and cold water immediately introduced, thus suddenly chilling the fluid material. If the exact point be missed, failure will result. Thus, if the pipes are colder than the inflowing paraffin wax, it will congeal as it touches the metal, assuming a dull, striated aspect. On the other hand, if the moulds are allowed to cool slowly, the candles will shrink on to, instead of from, the walls, and will be injured in removal from the moulds, if indeed they can be withdrawn at all in the solid state. When the operation is properly carried out, and the pipes are not worn by usage, and further, if the paraffin is highly refined and of a high melting-point, the candles leave the moulds with a lustre which hardly suffers by ordinary handling. This lustre, combined with the translucency, snowy whiteness, and ready adaptability to ornament in shape and colour, gives paraffin wax the pre-eminence over all other materials for candle making. It has, however, its disadvantages. The readiness with which it liquefies by heat, gives to even the best paraffin candles a tendency to 'gutter.' Moreover, the paraffin wax has the peculiar property, which is independent of the melting-point, of becoming plastic after exposure to a moderate degree of heat. The time required to develop this tendency varies, it is true, with the hardness or fusibility of the paraffin wax, which ranges from 105°F. to 140°F.; but even ceresin, of a melting-point of 142°–143°F., is affected by protracted heat. The inferior varieties of paraffin candles, from the ease with which their substance melts, are very prone to smoke; the wick is apt to be too abundantly supplied with combustible, and is consequently chilled below the point at which complete combustion can take place.

By judiciously mixing stearin and paraffin wax, the candle maker is able to obviate many of the defects of the substances, whilst retaining their advantages. Such candles as 'petrostearine,' 'palmitine,' and other popular varieties, and especially the paraffin candles of the Saxo-Thuringian paraffin-wax industry, are made on this principle.

One of the greatest improvements of the last decades in candle making is the self-fitting end, by which simple device a candle will fit any normally constructed sconce without being scraped or using paper or any other expedient to enlarge or diminish the butt. The self-fitting end patented by J. L. Field (Eng. Pat. 3032, 1861), is now in universal use. Fig. 5 gives an example of the conical butt, while Fig. 6 represents the machine patented by E. Cowles for its manufacture. The difficulty to be overcome lies in the butt projecting beyond the stem of the candle, which renders the ordinary method of withdrawal impracticable. To meet this, the butts are cast in a separate frame, which can be fitted to or removed from the pipes at will. When the machine is to be filled, the butt frame is lowered by the chain till the butts rest upon and fit tightly into their respective pipes. The wicks are then drawn through the butt moulds with a wire and clamped in a centric position,

FIG. 5.

after which the filling is proceeded with in the usual manner. When cold the wicks are cast loose, the tops scraped off, and the upper frame hoisted off the butts, as shown in the illustration, the operation being concluded as before. It will be noticed that this apparatus precludes running a continuous wick, as is done in the making of candles having plain ends; and in a large factory, a serious loss is incurred in the course of the year by the inch or two of wick snipped off at each operation. A very ingenious machine for saving this waste is due to E. Cowles, who invented a split bed-plate holding the butts. When ready for withdrawal, the butt moulds are raised and opened out by a simple lever motion, and the candles can thus be passed through without further trouble (Figs. 7 and 8).

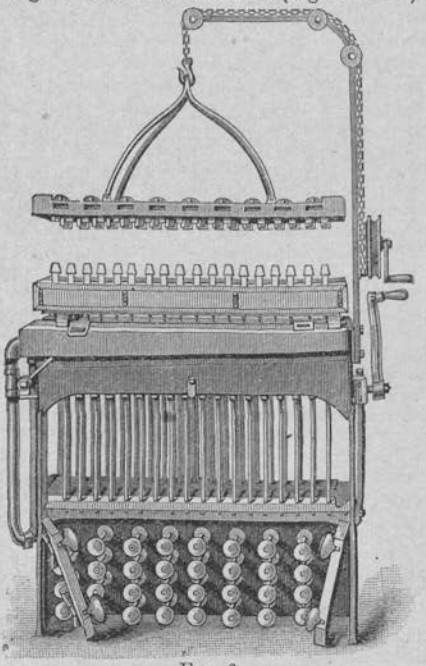


Fig. 6.

Numerous improvements have been made in recent years in the construction of candle machines by the makers in this country, in France, the United States, and Germany, but all these improvements refer to mechanical details only, without affecting the principle. All these machines work discontinuously. A continuous candle machine, for a description of which the reader must be referred to Engineering, 1901, Feb. 1st, has been constructed by Fournier et Cie, Marseille. The machine is very complicated, and would seem only to commend itself to works where a very large output can be relied upon, and where, at the same time, the works suffer from a shortage of cooling water.

An improvement, which has found more favour on the Continent than in this country, consists in perforating the stem of the candle longitudinally so as to afford an internal escape for any combustible which would otherwise have guttered down the outside. The up-draught of air which takes place in the tubes has a tendency to ensure more perfect combustion. By reason of the hardness required in their manufacture, these candles must be made with stearin.

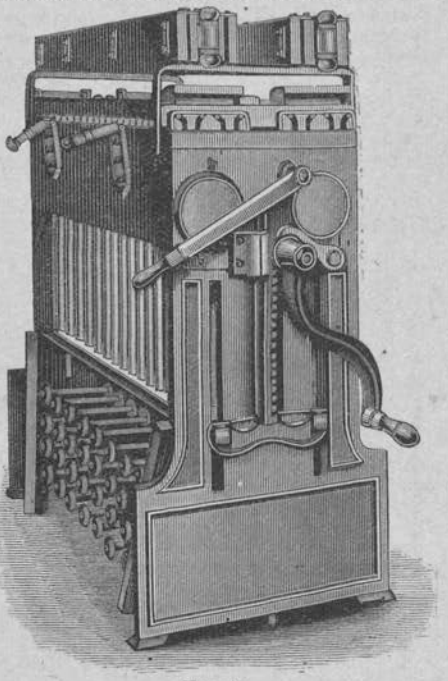


Fig. 7.

Candles made for ordinary purposes are ready for packing immediately after leaving the candle machine. Better class candles are subjected to polishing and finishing processes in special machines, which are much more used on the Continent than in this country.

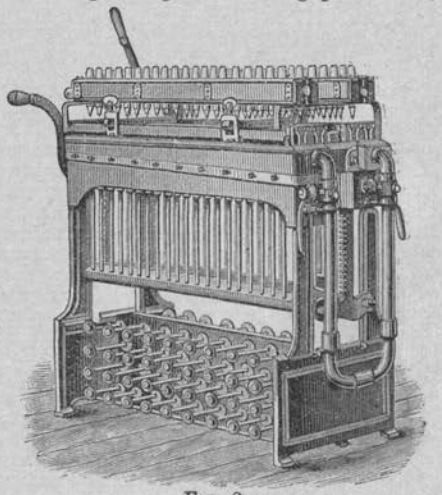


Fig. 8.

Much art has been expended on the ornamentation of candles. Before the introduction of aniline dyes, candles were coloured with such

pigments as vermilion, ultramarine, and verdigris; these, besides causing a dull, heavy appearance, ruined the wick by choking it with incombustible matter. In beeswax candles, this evil was minimised by confining the colour to the last coating, which, owing to the opacity of the beeswax, gave the appearance of a candle coloured throughout with but slight effect on the burning. The translucent paraffin, however, did not admit of this device. Paraffin candles are now coloured with coal-tar dyes by dissolving the dye in a small proportion of stearine which, when added to the paraffin, colours it to any desired shade. Of ornamented candles (Fig. 9), one of the most popular forms is the 'cable' or spiral pattern. This form, as patented by Field, was made by turning the plain candle in a lathe of complicated structure, which could fashion over thirty different sizes and patterns of candles, *e.g.* cabled, spiral, fluted, striped, &c. By grooving out continuous patterns, replacing the candle in its mould, and running in coloured stearin, a number of fanciful devices were obtained, each of which had their period of popularity. The 'King Alfred's candle,' the stem of which is divided by grooves of this kind into sections burning an hour each, still enjoys favour.

FIG. 9.

The demand for cabled candles is now so large that they are made in moulds, the pistons while ascending being caused to rotate, so as to screw the candles out of their spiral moulds.

Night lights are short thick cylinders of a fat or wax, furnished with small wicks, their object being to give a constant and lasting rather than a bright light. They are usually cast direct in paper cases, and are recommended to be placed on water. Price's Candle Co. have adopted the plan of casting the cylinders in a machine similar to a candle frame, and employing a material so hard (pressed cocoa-nut stearin) as to retain its form in hot weather without external support. These lights are burnt in glass cups, thus shedding their full light and rendering the precaution of water unnecessary. Another very popular form of this illuminant is Clark's 'pyramid' night light, which, as its name indicates, is coniform. In this, the material employed is pressed tallow of great purity, and the wick is a rush-pith with two lateral strips of the peel left adhering. These turn outwards in burning, giving a neat and shapely flame. The base of the cone is a disc of plaster of Paris, which holds the wick upright till the whole of the fat is consumed; a result achieved less surely in the other kinds, where the wick is of 'inkle' (flax), held by a little strip of tin, into which the base of the fibre is fixed.

The strides made in gas and electric illumination have not materially affected the prosperity of candle manufacture. On the contrary, every year sees a considerable increase in the number of candles made. This is especially due to the increasing consumption of candles in mines (Transvaal, India, Australia, &c.). An inquiry made by the writer, in 1903, as to the consumption of candle material in this country, led to an estimated quantity of 45,600 tons, which may be distributed over the different materials mentioned above, as follows: tallow (for dips), 1000 tons; stearin, 2190 tons; paraffin wax, 42,200 tons; ceresin, 100 tons. France produces about 30,000 tons of candles, chiefly stearin candles; Germany, about 11,000 tons, chiefly paraffin candles; Holland, about 6000 tons, chiefly stearin candles; Belgium, about 4000 tons, chiefly stearin candles. Austro-Hungary, Italy, and Russia produce much smaller quantities than the last-named countries.

J. L.

CANDLE-NUT OIL is obtained from the fruits of the candleberry tree, *Aleurites moluccana* (Willd), belonging to the family of spurgeworts (*Euphorbiaceæ*). The tree attains the height of 30 or 40 feet, is a native of the Moluccas and South Pacific Islands, and is widely distributed over the tropics of the eastern hemisphere; it also occurs in the Cameroons. In India it is known as 'Indian akhrout.' The fruits resemble walnuts in their appearance, but the shell of the candle-nuts is far thicker. The name 'candle-nut' is derived from the practice of the South Sea Islanders to dry the kernels, thread them on reeds, forming a candle, several of these candles being wrapped in a leaf of *pandanus* (screw-pine) so as to make a torch.

The average composition of the kernels is as follows:—

	Per cent.
Oil	61·0
Water	5·0
Albuminoids	23·0
Ash	3·4
Carbohydrates and crude fibre	7·6
	100·0

The cold-drawn oil is limpid, colourless, or yellowish; has a pleasant odour and bland taste, but cannot be used for edible purposes on account of its purging properties.

The oil is obtainable in enormous quantities, but hitherto it has not been used to such an extent as its drying properties would warrant.

The fruit of *A. triloba* (Forst.) is two-celled, fleshy, olive-coloured, and about two and a half inches in diameter. Each cell contains one nut, resembling in appearance and taste a walnut, the shell of which is very hard. The seeds yield about 50 p.c. of an oil known as 'kekuna oil.' Seeds from Hong Kong, where the tree is cultivated as one of the best shade trees, were found to contain 60 p.c. of an oil very similar to that obtained from *A. moluccana*.

J. L.

CANELLA BARK. The dried bark of *Canella alba* (Murr.), obtained from Florida and the West Indies in large buff-coloured quills or pieces of about an inch broad. Has a bitter pungent acrid taste and odour of a mixture of cloves and cinnamon, due to a volatile oil containing *eugenic acid* which is also found in oil of cloves. The bark contains a bitter principle, *canellin*, together with resin, mannite, and starch. Used in medicine as an aromatic bitter and tonic, and in rheumatism and gout.

CANELLE or **BISMARCK BROWN** *v.* AZO-COLOURING MATTERS.

CANNABIN or **INDIAN HEMP RESIN** *v.* RESINS.

CANNABINENE *v.* RESINS.

CANNABINOL. The active constituent of Indian hemp resin or 'hashish' (*v.* RESINS).

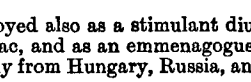
CANNABIS INDICA *v.* RESINS.

CANNONITE *v.* EXPLOSIVES.

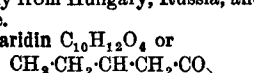
CANTHARIDES. *Spanish flies* (*Lytta vesicatoria*). Dried coleopterous insects used in medicine, in the form of plasters, tincture, liniments, &c., on account of their vesicating properties, due to a peculiar acrid principle, *cantharidin*.

Employed also as a stimulant diuretic, as an aphrodisiac, and as an emmenagogue. Obtained principally from Hungary, Russia, and the South of France.

Cantharidin $C_{10}H_{12}O_4$ or



(Spiegel, Ber. 26, 140), or



(Meyer, Monatsh. 1897, 18, 393), is obtained by treating the powdered insects with chloroform, ether, or ethyl acetate, acidified with sulphuric acid, and evaporating the extract and treating the residue with carbon disulphide or light petroleum, to remove fat; or by mixing the cantharides with water and magnesia; drying, treating with dilute sulphuric acid, and extracting with ether. The yield varies from 0·3 to 1·03 p.c. of the insects taken. Crystallises in trimetric plates, melts at 218°, but begins to sublime at 85°. It is tasteless and inodorous; blisters the skin strongly, especially when in solution or mixed with fat. Yields the alkaline salts of cantharidic acid $C_{10}H_{14}O_5$, by heating with aqueous solution of potash or soda.

CANTON'S PHOSPHORUS *v.* CALCIUM.

CAOUTCHOUC *v.* RUBBER; also TERPENES.

CAOUTCHOUC OIL. An oil which has proved efficient in preventing rust. It is spread with a piece of flannel in a very thin layer over the metallic surface which is to be preserved, and allowed to dry. To remove it, the article has simply to be treated with caoutchouc oil again, and washed after 12 to 24 hours (J. Soc. Chem. Ind. 1, 315).

CAP COMPOSITIONS *v.* EXPLOSIVES.

CAPE BERRY WAX *v.* WAXES.

CAPRIC ACID or **DECOIC ACID** *v.* DECATOIC ACID.

CAPROIC or **HEXOIC ACIDS** $C_5H_{11}\cdot COOH$. Seven isomerides are known.

1. *n-Caproic acid* $CH_3(CH_2)_4COOH$ occurs in the fats; in cheese; and, possibly, mixed with certain of its isomerides, in cocoa-nut oil; in St. John's bread; in the fruit of *Heracleum sphondylium* and in the flowers of *Satyrium hircinum*; and in the fusel-oil from the fermented molasses of mangel wurzel. Is best prepared by fractionating crude fermentation butyric acid (Lieben, Rossi, Annalen, 159, 75; 165, 118); b.p. 204·5°; sp.gr. 0·9446 at 0°.

2. *Isobutyl acetic acid*, or *γ-methylvaleric acid*

$$(CH_3)_2CHCH_2CH_2COOH$$

is present in butter; may be obtained by the action of hydriodic acid upon hydroxy*iso*caproic acid (Mielck, Annalen, 180, 57; Fittig, Rühlmann, *ibid.* 226, 347), or by the distillation of *iso*butylmalonic acid (König, Monatsh. 15, 20; Bentley and Perkin, Chem. Soc. Trans. 1898, 487); b.p. 200°–201°; sp.gr. 0·925 at 0°.

3. *Diethylacetic acid, pseudocaproic acid*, or *α-ethylbutyric acid* $(C_2H_5)_2CH\cdot COOH$, may be obtained by the action of sodium upon acetic ester, and treatment of the product by ethyl iodide (Frankland and Duppa, Annalen, 138, 221); by boiling diethylcarbinol cyanide with potassium cyanide (Saytzeff, *ibid.* 193, 349); by reduction of dichlorethyl acetic ester by sodium amalgam (Markownikow, Ber. 1873, 1175); by heating sodium ethylate and sodium acetate in a stream of carbon monoxide (Geuther and Fröhlich, Annalen, 202, 308); by heating diethylmalonic acid at 170°–180° (Conrad, *ibid.* 204, 141); by heating α-diethyl-β-hydroxybutyric acid (Schnapp, *ibid.* 201, 70); by heating diethylcyanacetic acid with concentrated hydrochloric acid at 160° (Hesse, *ibid.* 18, 749); b.p. 190° (756·5 mm.); sp.gr. 0·9196 at 20°/0°.

4. *Methylpropylacetic acid* or *α-methylvaleric acid* $CH_3\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CO_2H$ is obtained by the oxidation of its aldehyde, and by the reduction of methylacrylic acid (Lieben and Zeisel, Monatsh. 4, 37, 63); by heating α-methyl valerolactone or *iso*saccharin with hydriodic acid and red phosphorus (Liebermann and Scheibler, Ber. 1883, 1823; Kiliani, *ibid.* 185, 632); by heating α-methylpropyl-β-hydroxybutyric acid (Jones, Annalen, 226, 292); and by the distillation of turpentine; b.p. 193°–194°; sp.gr. 0·9279 at 18°/0°; 1 part water dissolves 0·5693 part at 17°.

5. *Methylisopropyl acetic acid, isocaproic acid*, or *αβ-dimethylbutyric acid*

$$(CH_3)_2CH\cdot CH(CH_3)CO_2H$$

may be formed from methyl*iso*propylcarbinol cyanide (Markownikow, Zeitsch. Chem. 1860, 205); by the oxidation of the corresponding hexylalcohol from Roman camomile oil (Köbig, Annalen, 195, 102), or by melting camphoric acid with caustic alkali (Crossley and Perkin, Chem. Soc. Trans. 1898, 16); b.p. 189°–191°.

6. *Dimethylethylacetic acid* or *αα-dimethylpropionic acid* $(CH_3)_2C(C_2H_5)CO_2H$ is formed by the action of hydrochloric acid upon dimethylethylcarbinol cyanide (Wischnegradsky, Annalen, 174, 56), and by the oxidation of the methylethyl ketone prepared from pinacolin (Lawrinowitsch, *ibid.* 185, 126). A colourless liquid; b.p. 187°, m.p. −14°.

7. (*a*) *β-ethylbutyric acid* or *active caproic acid* $CH_3\cdot CH(C_2H_5)CH_2COOH$ is obtained by the oxidation of the active hexylalcohol obtained from Roman camomile oil (Romburgh, Rec. trav. chim. 5, 221; Köbig, Annalen, 195, 102); b.p. 196°–198° (770 mm.); sp.gr. 0·930 at 15°.

(*b*) *Inactive β-ethylbutyric acid* may be formed by heating secondary butylmalonic acid (Romburgh, Rec. trav. chim. 6, 153) or from secondary butyliodide, diethylmalonic ester and sodium ethoxide (Kuhlisch, Monatsh. 14, 561; Bentley, Chem. Soc. Trans. 1895, 267).

CAPRYL ALCOHOL *v.* OCTYL ALCOHOL.

CAPRYLIC ACID *v.* OCTOIC ACIDS.

CAPSAICIN *v.* RESINS.

CAPSICUM (*Bird pepper, Cayenne pepper*). The dried ripe fruit of *Capsicum minimum* (Roxb.), which was probably a native of tropical

America, but is now known only in cultivation, the chief supply coming from Africa and India.

The fruit is 1–2 cm. long and about one-third as broad; somewhat flattened oblong-ovoid in shape, and is covered with a crimson or scarlet, semi-transparent, wrinkled coriaceous epicarp. It is two-celled and contains about 20 yellow, flat, reniform seeds, 3·5 mm. long and 2·5 mm. broad. It is prepared for use by grinding the whole fruit.

Cayenne pepper is sometimes adulterated with flour, corn-meal, or even sawdust. Entire capsicum is also frequently substituted by larger varieties. Adulteration of the powder may be detected by the estimation of oleo-resin, which should be not less than 5 p.c.; and of the ash, which should not exceed 7 p.c., and by microscopical examination (*v.* Bitto, Chem. Soc. Abstr. 1893, D, ii. 546).

The active principle of capsicum is *capsaicin* (*capsicin, capsicol*) $CH_3O{\cdot}C_{17}H_{24}NO{\cdot}OH$, which is present to the extent of 0·05–0·07 p.c. (Mörbitz, Chem. Zentr. 1897, ii. 593). It is obtained from the ethereal extract of capsicum, and crystallises from light petroleum in colourless plates, m.p. 63·5°, easily soluble in ether, alcohol, chloroform, &c., but almost insoluble in hot water and insoluble in cold water. It is not volatile in steam, and has the properties of a weak, phenol-like acid. The benzoyl derivative forms silky needles, m.p. 74° (Micko, Chem. Zentr. 1899, i. 293).

The other constituents are a volatile, non-acrid alkaloid; red colouring-matter; wax; resin; fixed oil; oleic, palmitic, and stearic acids; and a minute amount of a volatile oil having the odour of parsley (Pabst. Arch. Pharm. 230, 108).

Capsicum is largely employed as a condiment. In medicine, it is used, externally as a powerful rubefacient, and internally in the treatment of atonic dyspepsia, chronic alcoholism, and delirium tremens.

CAPSICUM RESIN *v.* RESINS.

CAPUT MORTUUM. A term employed by the alchemists to denote the residue remaining in the retort or alembic after the volatile matter had passed away.

CARAGHEEN MOSS. *Irish pearl moss* (*Chondrus crispus*) (*v.* CARRAGEEN; ALGÆ).

CARAJURU, CARCURU, or **CRAJURU.** A Brazilian dyestuff of a red colour, said to be identical with *chica-red*, used by certain Indian tribes to stain their skins, and which is obtained from the leaves of the *Bignonia chica* (Humb. et Bonpland). It is a light, mealy, odourless, tasteless powder, which acquires a coppery lustre on trituration. Insoluble in water, but soluble in alcohol, ether, and alkalis (Virey, J. Pharm. 1844, 151).

CARAMEL. The brown substance produced by the action of heat on sugar or glucose, and used for colouring liquors, sweetmeats, and gravies. According to Stolle (Chem. Zentr. 1899, ii. 1021), it has the composition $C_{12}H_{18}O_9$, and is formed from sugar by the elimination of $2H_2O$, and is thus identical with the *caramelan* of Gélis. Cryoscopic observations by Sabanéeff and Antushevitch (J. Russ. Chem. Soc. 25, 23), would seem to indicate that its molecular weight is much higher than this formula implies. They point out that carbon dioxide is given off in its formation, and that it is not a carbohydrate, but has the composition $C_{126}H_{188}O_{80}$. They represent its production from sugar by the equation:

$$11C_{12}H_{22}O_{11}=C_{126}H_{188}O_{80}+7CO_2+27H_2O.$$

Properties.—Amorphous, reddish-brown, brittle mass; porous and deliquescent; completely soluble in water, partially soluble in alcohol; of a bitter taste and non-fermentable. Melts at 134°–136°.

Preparation.—Common sugar is heated, with constant stirring, in a metal pan capable of containing about ten times the quantity taken, till the whole mass melts, turns brown, and at last suddenly froths up, when the heat must be immediately stopped. During the heating, much water and a little acid escape, but no permanent gas. Not more than 15 p.c. of the weight of the sugar should be driven off, as the product is liable to become insoluble if further heated.

For preparation of caramel colours, Asrymusry recommends the following processes (long kept secret):—

Colour for rum.

Potassium or sodium hydroxide .	3 kilos.
Water	6 „
Or potassium or sodium carbonate .	4 „
Water	8 „

Dissolve with heat in large iron pan, and add

Glucose	120 kilos.
Or syrup of glucose . . .	130 „

Boil over the fire till irritating vapours begin to appear, then decrease the heat and stir continuously till the required shade is produced, then stop the process by adding 30 to 40 litres of water in a fine jet.

Colour for beer or vinegar.

Ammonium carbonate . .	6 kilos.
Water	6 „
Glucose	120 „

Process exactly as above.

Detection of caramel in wines, &c.—10 c.c. of the liquid to be tested is mixed with 30 to 50 c.c. of paraldehyde, and enough alcohol added to make the liquids mix; if caramel is present, it forms a dirty-brown precipitate sticking to the bottom of the vessel; the solution is poured off, the precipitate washed with alcohol dissolved in a little hot water, and the solution evaporated to 1 c.c., when different quantities of caramel may be compared by comparison of colours to confirm; this solution is mixed with one of 2 parts hydrochloride of phenylhydrazine in 20 of water, with excess of acetate of soda. Caramel yields an amorphous brown precipitate.

According to Magalhaës (Compt. rend. 1896, 123, 896), caramel prepared from cane sugar differs considerably from caramel made from glucose, in that it behaves with certain reagents exactly like a coal-tar colour. Thus, when treated with basic lead acetate and then shaken with amyl alcohol, the former caramel communicates an orange-yellow colour to the solvent, whilst with glucose caramel, no colouration occurs. Ether, when shaken with a solution of the former, acquires an orange-yellow colour, whilst with the latter no colour is extracted. Mordanted wool is dyed orange by the former, yellow by the latter. Genuine wine, to which no caramel has been added, does not give these

reactions (C. f. D'Aquiar and Da Silva, Compt. rend. 1897, 124, 408).

Rough test for caramel in beer.—Add a quantity of tannic acid, and shake thoroughly. If malt only is present, the colour is precipitated. Caramel colour remains unchanged.

Little is known of the chemistry of caramel. Gélis separated it into three amorphous substances, *caramelan*, *caramelen*, and *caramelin*, differing in solubility and colouring power, but not of fixed composition. Stolle, by heating caramelan with dilute (3 p.c.) hydrochloric acid, obtained a hexose, which gave an osazone crystallising in yellow needles, melting at 197°. Fradiss (Chem. Zentr. 1899, i. 1160) determines the amount of caramel in sugar products by treating the dry substance with methyl alcohol of 95°, evaporating on the water-bath, drying the residue *in vacuô*, or in a current of dry air, and again digesting it with methyl alcohol for 2 hours. The caramel is precipitated from the solution by amyl alcohol, the precipitate redissolved, reprecipitated once or twice more, and finally dried at 90° and weighed. The caramel may also be determined by titrating with Fehling's solution, but if dextrose is present, it is necessary to titrate the original solution before and after treating with excess of lead acetate. Then if A=c.c. of copper solution required, a=c.c. of original solution required for 5 c.c. of copper solution, the volume of the copper solution, corresponding with the caramel, is $5\ (a-A)$. Allowance must also be made for the amount of lead acetate solution ($\frac{1}{15}$ vol.) used. The dextrose may also be destroyed by boiling with calcium carbonate and then precipitating with carbon dioxide. Traces of caramel are estimated by treating 200 c.c. of the solution with excess of ammoniacal lead acetate. The precipitate, after washing with water free from carbonic acid, is suspended in water and decomposed with hydrogen sulphide. The filtrate is again treated with lead acetate, and the solution, from which the hydrogen sulphide has been expelled by evaporating to 10 c.c., is treated with copper solution.

Stolle (Chem. Zentr. 1899, ii. 1099) bases a method of determining caramel by means of the spectroscope on the fact that aqueous solutions of that substance partially absorb the rays of the blue end of the spectrum. The results are said to be accurate to within 0·05 p.c.

Methods for estimating the amount of caramel on the surface of coffee berries roasted with sugar, have been suggested by Neubauer, König, Stutzer, and Hilger. These methods have been tested by Fresenius and Grünhut (Zeitsch. anal. Chem. 1897, 36, 225), who give the preference to the method of Hilger.

Stutzer's method, which consists in shaking 10 grams of the unground coffee for 5 minutes with 250 c.c. of cold water, making up to 500 c.c., decanting, filtering, and determining the solid contents (dried at 100°), and the ash, was recommended by the Conference of Bavarian Technical Chemists. Neubauer's and König's processes, which depend on the extraction of the berries with hot water, give too high results.

In Hilger's process, 10 grams of whole coffee are digested three times for half an hour each time, with 100 c.c. of a mixture of equal vols. of water and 90 p.c. alcohol at ordinary temperatures. Each portion of the extract is decanted, and the united extracts are made up to 500 c.c., filtered, and residue and ash determined. If, from the numbers thus obtained, there is deducted a constant 11·07 of dry residue, or 0·83 of ash-free residue per 100 grams of dry coffee, the remainder represents the amount of caramel present.

CARANNA *v.* OLEO-RESINS.

CARAPA BARK. The bark of *Carapa Guianensis*, has a bitter taste, and is used as a febrifuge. Said to contain an alkaloid, carapine (Petroz and Robinet, J. Pharm. 7, 293, 349).

CARAPA OIL. 'Carap Oil' or 'Crab Oil' (Fr. *Huile Carape*), is obtained from the seeds of the 'carap,' 'crappo' or 'crab-wood' tree, *Carapa Guianensis* (Aubl.), a native of the West Indies and Central America.

The oil is prepared in Trinidad for local consumption by very primitive methods. According to de Verteuil (Trinidad, London, 1858, 272), the seeds are gathered in June and July, boiled for 6 hours, then laid in heaps for 8 or 10 days, during which time they undergo a sort of fermentation; they are then broken, and the pulp they contain carefully taken out and kneaded into lumps of thick paste, each about 15 lbs. This paste is laid on boards slightly incurvated and inclined, and placed in a sheltered place, when the oil oozes through the mass, and runs into a vessel placed for its reception. The paste is carefully remoulded every morning and evening, so as to favour the disengagement of the oil. After 12 days, boiling water is poured on the mass, and a fresh quantity of oil of inferior quality is thereby obtained. It is a clear yellow oil with a faint vegetable odour, and an intensely bitter taste which precludes its use as an edible oil. It is used locally as an embrocation against rheumatism and for the destruction of ticks which attack domestic animals (de Verteuil, The Agricultural Record, Trinidad, August, 1899, 17). It has considerable reputation as a liniment for dressing wounds on horses and cattle. Its excessive bitterness repels all insects, and mixed with tar is used for preserving wood. It is well suited for the manufacture of soap, and it is in this direction that its future possibilities lie.

The oil from *C. grandiflora*, from Uganda, has been examined by Lewkowitsch (Analyst, 1908 33, 184). Good kernels contained 30·26 p.c. of oil. The colour of the cold-pressed oil was almost white, with a tinge of pale yellow. At the ordinary temperature, it solidifies. The hot-pressed oil is much darker in colour, and remains solid at the ordinary temperature.

Lewkowitsch (Analyst, 1909, 34, 10) has also examined the oil from *C. procera* (D.C.), the seeds being obtained from Sierra Leone. The sound kernels yielded by extraction with ether 57·26 p.c. of oil; whilst the yield of oil by cold and hot extraction at a pressure of 150 atmospheres was 46·7 p.c.

The following analytical results are due to C. H. Wright (Bull. Dept. Agric. Trinidad, ix. 1910):—

	I.	II.
Specific gravity at 40°/40°C.	0·9149	
Specific gravity at 15·5°/15·5°C.	0·9249	0·9211
Acid value . . .	27·5	19·4

	I.	II.
Saponification value	197·2	196·1
Iodine value	67·7	58·5
Reichert Meissl value	3·8	3·6
Unsaponifiable matter	—	1·16

CARAWAY OIL *v.* OILS, ESSENTIAL.

CARBAMIC ACID CH_3NO_2 or NH_2COOH. *Aminoformic acid.* An acid not known in the free state. *Ammonium carbamate* is, however, met with in freshly sublimed commercial ammonium carbonate, and may be prepared by mixing gaseous ammonia and carbon dioxide. Obtained also by the action of alkaline solution of potassium permanganate on albumen, leucine, tyrosine, and glycocoll.

CARBAZOLE $C_{12}H_9N$ or $\langle C_6H_4 \rangle NH$. A white crystalline substance found amongst the products of the distillation of coal tar, and also met with in crude anthracene. Carbazole compounds are most easily recovered from crude anthracene by converting the former into the easily soluble nitrosocarbazole (Wirth, Eng. Pat. 14462; J. Soc. Chem. Ind. 1901, 464). May be obtained by passing vapour of aniline or diphenylamine through a red-hot tube; by boiling iminodiphenyl sulphide $HN\langle C_6H_4 \rangle S$ with reduced copper; by passing the vapour of orthoaminodiphenyl over time heated to a dull redness (Blank, Ber. 1891, 306); or by acting on orthoaminodiphenylamine with nitrous acid and heating the phenylazimidobenzene so formed to 360° (Graebe and Ullmann, Annalen, 291, 16). Forms white laminæ; m.p. 238°, b.p. 351·5° (corr.). Carbazole dissolves in concentrated sulphuric acid to a yellow solution, which changes to red-violet on heating. Addition of formaldehyde gives a blue solution, changing to a greenish blue on addition of large quantities (Gabretti, Chem. Zentr. 1907, ii. 98). 1 mol. carbazole, 2 mols. salicylaldehyde and concentrated sulphuric acid, heated to 100°–110°, give an intense blue colour (Carrara, Gazz. chim. ital. 1899. ii. 535).

By melting together carbazole and oxalic acid, and extracting with hot water and benzene, dissolving the residue in warm alcohol, filtering and evaporating, *carbazole blue* is obtained. The alcoholic solution of carbazole blue, when treated with glacial acetic acid and zinc-dust, is decolourised. Filtered into caustic soda solution, the leuco- base separates out as a white flocculent precipitate. On oxidation with any of the usual reagents, the blue colouring matter is again formed (Bamberger and Müller, Ber. 1887, 1903; J. Soc. Chem. Ind. 1887, 660). *Carbazole yellow* is prepared from the tetrazo- derivative of diaminocarbazole. It is easily soluble in water, and dyes unmordanted cotton in a neutral bath a fast golden yellow, and wool in a neutral or acid-bath a yellow, fast to milling (Bad. Anil. and Sod. Fab. Eng. Pat. 14478 and 14479; J. Soc. Chem. Ind. 1889, 771) (*v.* AZO- COLOURING MATTERS).

Nitrocarbazole is obtained by treating nitrosocarbazole with 10 times its weight of benzene and its own weight of nitric acid; sp.gr. 1·36 (Wirth, Eng. Pat. 2899; D. R. P. 128853; J. Soc. Chem. Ind. 1901, 890). Dinitrocarbazoles, *v.* Bad. Anil. u. Sod. Fab. (D. R. P. 46438; Frdl. ii. 447); Wirth (D. R. P. 128853; Frdl. vi. 58). These nitro- compounds may be reduced to the amino- compounds by means of alkali sulphides (Wirth, D. R. P. 139568; Chem. Zentr. 1903, i. 746). By heating carbazole with concentrated sulphuric acid, a mixture of disulphonic and trisulphonic acids is obtained. Nitration and subsequent reduction of the former yields aminocarbazoledisulphonic acid, which, when diazotised and coupled with β-naphthol, yields a dyestuff dyeing red from an acid-bath. If the nitric acid is added direct to the products of sulphonation, on reduction a second amino- acid is obtained which, when diazotised and coupled with β-naphthol, gives a red dyestuff, and with α-naphthylamine a violet (Schultz and Hauenstein, J. pr. Chem. 1907, 336). The sulphonic acids, preferably the disulphonic, condense with tetralkyldiaminodiphenylcarbinol to yield valuable green dyestuffs (Cassella & Co. Eng. Pat. 20709; J. Soc. Chem. Ind. 1909, 697). By allowing nitrosophenol, its homologues or derivatives to act on carbazole in the presence of conc. sulphuric acid, compounds are obtained which yield blue sulphide dyestuffs with alkali polysulphides (Haas, Eng. Pat. 2918; J. Soc. Chem. Ind. 1909, 517).

A method has been patented (Ch. Fab. Act. Gesell. in Hamburg, D. R. P. 81237; Ber. 1895, iv. 692) for obtaining potassium cyanide or ferrocyanide, by heating the potassium derivative of carbazole in the absence or presence of an iron salt.

CARBITE. An explosive consisting of nitroglycerine (25), potassium nitrate (34), flour (38·5), barium nitrate (1), powdered bark (1), and sodium carbonate (0·5 part).

CARBODYNAMITE *v.* EXPLOSIVES.

CARBOHYDRATES. The term is applied to polyhydroxy-aldehydes and ketones, and to the substances which give these when hydrolysed by heating with mineral acids. Dextrose, ordinary sugar or sucrose, starch, and cellulose are carbohydrates universally distributed in plants. Dextrose and glycogen enter into the composition of animal tissues. The simple carbohydrates, monosaccharides, have the empirical composition CH_2O, the most important being those containing 5 or 6 atoms of carbon. The complex carbohydrates, polysaccharides, are built up from two or more simple carbohydrates with the elimination of water; they have the composition $(C_6H_{10}O_5)_nH_2O$ (Kiliani, Chem. Zentr. 1908, 32, 366). Compounds in which n equals 1, 2, 3, or 4 are distinguished by names having the suffix *-ose.* They may be conveniently grouped as follows:—

1. Monosaccharides.

(*a*) Pentoses $C_5H_{10}O_5$, *e.g.* arabinose, xylose.

(*b*) Hexoses $C_6H_{12}O_6$, aldoses, *e.g.* dextrose, mannose, galactose; ketoses, *e.g.* lævulose, sorbose.

2. Disaccharides: $n=2$. $C_{12}H_{22}O_{11}$.

(*a*) Non-reducing, *e.g.* sucrose, trehalose.

(*b*) Reducing, *e.g.* maltose, lactose, &c.

3. Trisaccharides: $n=3$. $C_{18}H_{32}O_{16}$. Gentianose, raffinose, melezitose.

4. Tetrasaccharides: $n=4$. $C_{24}H_{42}O_{21}$. Stachyose.

5. Polysaccharides:

(*a*) Glycogen, inulin, dextrins, n unknown.

(*b*) Starch, cellulose n very large.

Related to the carbohydrates are those substances which yield simple carbohydrates, together with other substances when hydrolysed. Such are glucosides, gums, pectins, &c. (*q.v.*).

General characters.—The members of classes 1, 2, 3, 4, and 5*a* are soluble in water. They have a more or less pronounced sweet taste. The monosaccharides are colourless crystalline compounds, characterised by the power of reducing alkaline solutions of the heavy metals, for example, copper. They form characteristic compounds with phenylhydrazine.

The di- and poly-saccharides are converted into simple carbohydrates when hydrolysed. This change may be effected by means of mineral acids, or, as a rule, more quickly by enzymes. The complicated polysaccharides are usually amorphous; they tend to form colloidal solutions, and are chemically relatively inert. In virtue of the hydroxyl- groups which they contain, they react with acetyl chloride, benzoyl chloride, nitric acid, &c., forming esters.

Carbohydrate solutions are generally optically active. The direction and amount of the rotation vary with the substance, and also with the strength of the solution, the nature of the medium, the temperature, &c. The optical rotatory power of carbohydrates is made use of in their analyses (*v.* SACCHARIMETRY).

Constitutional formula of Dextrose.—In addition to those carbohydrates which occur naturally, a number of others have been prepared artificially by Emil Fischer, and it is largely to his work that the present complete knowledge of the group is due. (Fischer's original work has been republished, Untersuchungen über Kohlenhydrate, Berlin, 1909, J. Springer.)

Dextrose and its isomerides $C_6H_{12}O_6$, conveniently termed glucoses, have 5 oxygen atoms present as 'hydroxyl,' since they form esters such as dextrose pentacetate

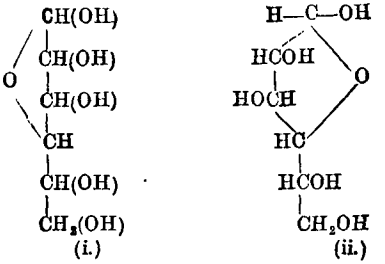
$$C_6H_7O(O\cdot CO\cdot CH_3)_5.$$

The sixth oxygen behaves as an aldehyde in dextrose and galactose, as a ketone in lævulose and *sorbose*. The two classes of compounds are accordingly referred to as aldoses and ketoses. Reduction converts the glucoses into alcohols $C_6H_{14}O_6$, dextrose yielding sorbitol and mannitol, and galactose forming dulcitol. Secondary hexyliodide, a derivative of normal hexane, is formed by the action of hydrogen iodide; hence the glucoses must possess all their six carbon atoms united in a normal chain.

Dextrose on oxidation yields, in the first place, gluconic acid $C_5H_6(OH)_5\cdot CO_2H$ which retains all six carbons and, like dextrose, forms a pentacetyl ester. Further oxidation converts it into saccharic acid $C_6H_{10}O_8$. Galactose behaves similarly, yielding the isomeric, galactonic, and mucic acids. Taking further into consideration the reducing power of dextrose, the constitutional formula may be written:

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO.$$

This formula does not fully express the behaviour of dextrose, which lacks many of the well-attested properties of the aldehydes; for example, it is not oxidised in the air, and does not show their various colour reactions. Tollens, in 1883, therefore, proposed the lactonic or γ-oxide formula (i.), which may be also written (ii.):



This formula (i. or ii.) is in entire agreement with the reactions of dextrose, and has been generally adopted. It is supposed that in presence of alkalis and other reagents the γ-oxide ring opens, forming the aldehyde.

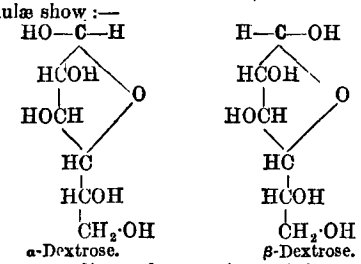
The work of Tanret (Compt. rend. 120, 1060) has shown that dextrose exists in more than one form. In addition to the hydrated and anhydrous modifications, he isolated two other anhydrous modifications. These differed particularly in optical rotatory power. Tanret described an α-dextrose having $[\alpha]_D+110°$ when first dissolved, and falling in aqueous solution; a β-dextrose having $[\alpha]_D+19°$, and increasing in solution; and a γ-dextrose having $[\alpha]_D+52{\cdot}5°$, and remaining constant in solution. It had long been known that the optical rotatory power of freshly dissolved dextrose diminished to about one-half its initial value in solution, and the term *muta-rotation* or *bi-rotation* was applied to this phenomenon.

Dubrunfaut ascribed the change to purely physical causes. Fischer considered that the aldehyde dextrose underwent hydration to an alcohol $C_6H_{14}O_7$ of lower rotatory power. In view of Tanret's discoveries, it is now considered that the change in rotatory power is due to the mutual interconversion of the α- and β-dextroses, until equilibrium is attained. γ-Dextrose represents such an equilibrium mixture. It is supposed that both α- and β-dextrose have a closed γ-oxide ring structure, and it is still a matter of controversy whether some proportion of open-chain aldehyde is present in solution in the equilibrium mixture. (For the full discussion of this question, *see* E. F. Armstrong's The Simple Carbohydrates, Longmans, 1910.)

To understand fully the relation of α- to β-dextrose, it is necessary to refer to the van't Hoff-Le Bel conception of space isomerism. Chemical compounds which rotate the plane of polarised light contain an *asymmetric carbon atom*, that is, one in which the four affinities are satisfied by four distinct radicles. Such a carbon atom is considered as lying in the centre of a tetrahedron, and each of the four different radicles with which it is combined as being at the four solid angles thereof. Two modifications of the compound are possible, which are related to one another like an object and its reflected image.

In the Tollens formula for dextrose, the carbon atom (C) has the four different groups, H, OH, the oxygen of the ring, and the complex $C_5H_{10}O_4$ attached to it. It is asymmetric, and two isomerides are possible, which are represented on a plane surface by writing H and OH on one

or other side of the carbon atom, as the following formulæ show :—

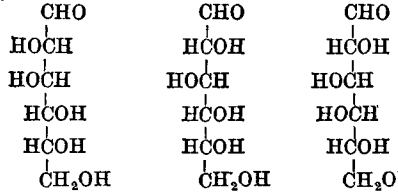


Corresponding to these two isomeric forms, dextrose gives rise to a double series of derivatives.

The compound represented by the formula $CH_2(OH)\cdot\overset{*}{C}H(OH)\cdot\overset{*}{C}H(OH)\cdot\overset{*}{C}H(OH)\cdot\overset{*}{C}H(OH)\cdot CHO$ contains four asymmetric carbon atoms (marked *), and should, therefore, be capable of existing in 16 stereoisomeric forms, 8 of which would be mirror images of the other 8, and of equal but opposite rotatory power.

The carbohydrate group has afforded a unique opportunity of testing this hypothesis, and although only three of the isomerides occur naturally, no less than 12 have been prepared artificially by Fischer, who has, in addition, made them in such ways that their structure is established.

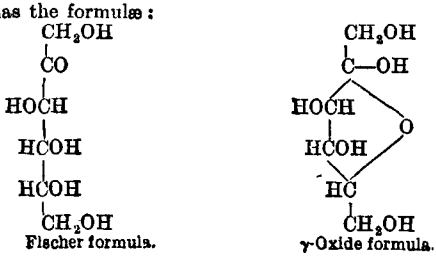
The known aldohexoses are the dextro- and lævo- isomerides of mannose, dextrose, idose, gulose, galactose, and talose. It will suffice to give the constitutional formulæ as established by Fischer of the natural members :



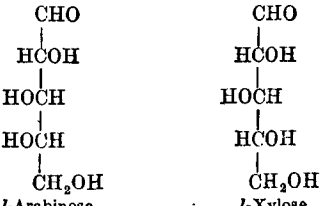
Mannose and galactose, like dextrose, exist in α- and β- forms, and it is more correct to write their formulæ in the form adopted for α- and β-dextrose.

As is to be expected, the isomeric glucoses differ but little in their chemical behaviour.

Formula of Lævulose.—Lævulose, when oxidised, forms glycollic and trihydroxyglutaric acid, or other acids with less than 6 carbon atoms. It forms an additive compound with hydrogen cyanide, which yields lævulose carboxylic acid $C_7H_{14}O_8$ on hydrolysis; and this, when boiled with hydriodic acid, is converted into methylbutylacetic acid $C_4H_9\cdot CHMe\cdot CO_2H$. This behaviour establishes lævulose as a ketohexose. It has the formulæ :



Formulæ of the Pentoses and Tetroses.—Eight aldopentoses are possible, of which six have been artificially prepared, viz. *d*- and *l*-arabinose and xylose, *d*-lyxose, and *l*-ribose. The two naturally occurring pentoses have the constitutional formulæ :



Like dextrose, they occur in two forms, and are more correctly written with a γ-oxide structure. A pentose believed to be *d*-arabinose has been isolated from the glucoside barbaloin (Léger). Levene (Ber. 1909, 42, 3247; 1910, 43, 3147) claims to have obtained *d*-ribose from nucleic acid, but this is disputed by Neuberg.

Three out of the four possible aldotetroses are known, viz. *d*- and *l*-erythrose and *l*-threose, but they have not been found in nature.

Reaction with Phenylhydrazine.—The behaviour of the carbohydrates with phenylhydrazine is particularly characteristic, and it has further an historical interest, as phenylhydrazine, in the hands of Fischer, served as one of the chief aids in the elucidation of the relationships of the group.

Dextrose reacts with the reagent in acetic acid solution in two *stages*. In the cold a phenylhydrazone is formed :

$$C_6H_{12}O_6+C_6H_5\cdot NH\cdot NH_2 = C_5H_{11}O_5\cdot CH:N\cdot NH\cdot C_6H_5+H_2O.$$

This is a colourless substance, soluble in water, and is obtained in two modifications, one or the other predominating according to the method of preparation. Similar compounds, with asymmetrically disubstituted hydrazines—for example, benzylphenylhydrazine—are often less soluble and more characteristic. Mannose is remarkable in forming an almost insoluble phenylhydrazone. The hydrazones of lactose and maltose are very soluble.

At the temperature of boiling water, dextrose reacts with excess of phenylhydrazine to form the phenylosazone

$$CH_2(OH)\cdot[CH(OH)]_3\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$$

Dextrose (1 molecule) is heated with 3–4 molecules of phenylhydrazine, which should be almost colourless, and free from oxidation products, and an equal volume of 50 p.c. acetic acid in a flask immersed in boiling water for an hour or more. Usually the osazone begins to separate in 20 minutes or less. In the case of the disaccharides, no separation of osazone takes place from the hot solution.

The yellow osazone is filtered and carefully washed; it may be crystallised from most organic solvents, but the most suitable appears to be a dilute solution of pyridine. Dextrose, mannose and lævulose form the same phenyl osazone, as they differ only in the relative positions of groups which are destoyed in the formation of the osazone.

Too much dependence must not be placed on the melting-points of the osazones in identifying unknown sugars in solution, as these depend

very largely on the rate of heating, and the method of purification adopted. Disubstituted hydrazines do not directly form osazones with dextrose, though these may be prepared from the osones.

To recover the original sugar from the phenylhydrazone, it is boiled in water with a slight excess of benzaldehyde. The phenylhydrazine is removed as benzaldehyde phenylhydrazone, the excess of aldehyde extracted by ether, and the sugar solution concentrated *in vacuó*. With the disubstituted hydrazones better results are obtained on using formaldehyde.

The phenylhydrazine residues may be removed from the osazones by heating with fuming hydrochloric acid. Compounds termed osones are formed:

$$CH_2(OH)\cdot[CH\cdot(OH)]_3\cdot CO\cdot CHO.$$

These are colourless syrups; they act as strong reducing agents, combine directly with phenylhydrazine, and are non-fermentable. The slightly soluble osazones of the disaccharides, and of the pentoses, are converted into osones on boiling with benzaldehyde.

When reduced by means of sodium amalgam, the osones are converted into ketoses, and not into the aldoses from which they were formed. Thus it is possible to pass from dextrose to lævulose—a transformation of great importance—the stages being:

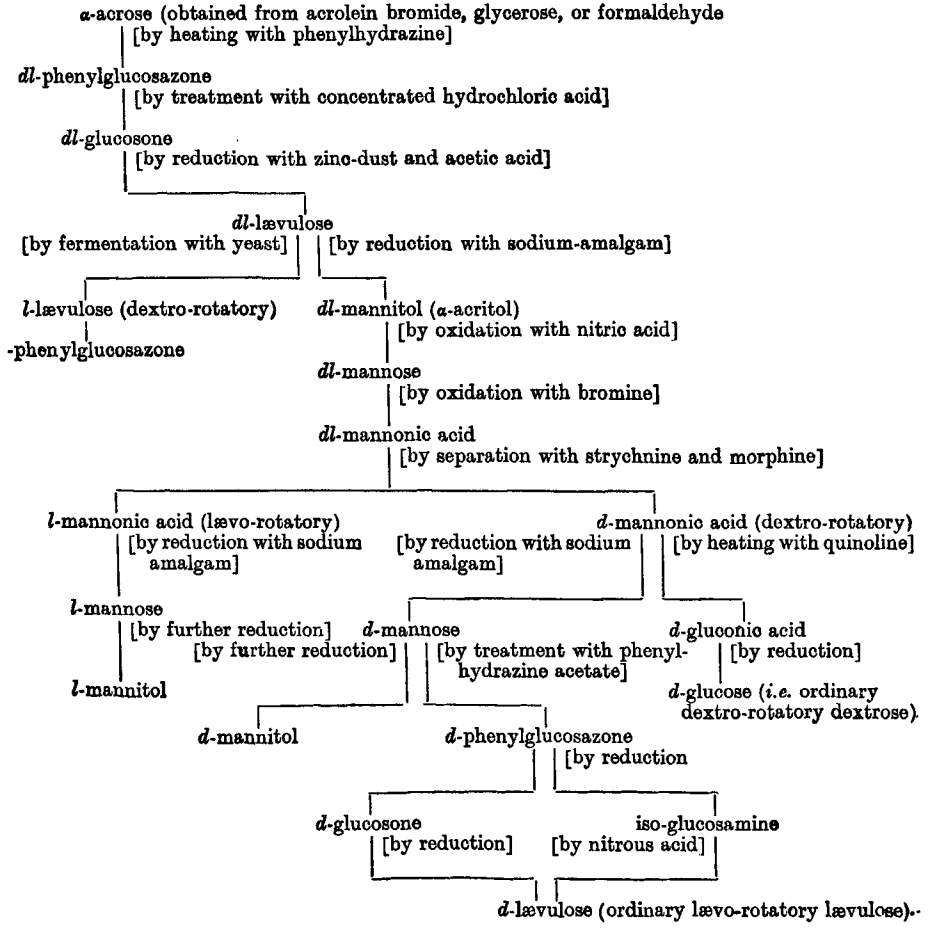
dextrose → phenylosazone → osone → lævulose.

Another important transformation is that from dextrose to mannose, which is based on the fact that gluconic acid (*q.v.*), when heated with quinoline, is converted into a mixture of gluconic and mannonic acids. The stages in this case are:

$$\text{Dextrose} \xrightarrow{\text{oxidation}} \left\{\begin{matrix}\text{gluconic}\\ \text{acid}\end{matrix}\right\} \rightarrow \left\{\begin{matrix}\text{mannonic}\\ \text{acid}\end{matrix}\right\} \xrightarrow{\text{reduction}} \text{mannose}$$

By the aid of these two reactions, Fischer was able to pass from the synthetical *a*-acrose to *d*-glucose, *d*-fructose, and *d*-mannose, and so effect the complete synthesis of the naturally occurring hexoses.

The following scheme shows the successive operations:—



Cyanohydrin synthesis.—The aldoses combine directly with hydrogen cyanide, forming nitriles, which, when hydrolysed, give rise to acids containing one carbon atom more than the original

carbohydrate. The lactones of these acids, when reduced with sodium amalgam, yield the corresponding aldoses with one carbon atom more than the original carbohydrate:

$C_5H_{11}O_5\cdot CHO + HCN = C_5H_{11}O_5\cdot CH(OH)\cdot CN \rightarrow$
$C_5H_{11}O_5\cdot CH(OH)\cdot CO_2H \rightarrow C_5H_{11}O_5\cdot CH(OH)\cdot CHO.$

In this manner arabinose is converted into dextrose, dextrose into glucoheptose. Fischer has continued the process as far as the aldononose.

Actually two isomerides are formed at each stage, and arabinose gives both dextrose and mannose.

Degradation.—The converse change from dextrose to arabinose has been effected by two different methods.

Wohl (Ber. 1893, 26, 730, &c.) heated dextrose oxime with concentrated sodium hydroxide, so converting it into gluconic acid nitrile, from which, on further heating hydrogen cyanide was eliminated and *d*-arabinose formed

$C_5H_{11}O_5\cdot CHO \rightarrow C_5H_{11}O_5\cdot CH{:}N\cdot OH \rightarrow$
$C_5H_{11}O_5\cdot CN \rightarrow C_5H_{10}O_5.$

In practice the method adopted is to heat the oxime with acetic anhydride and a grain of zinc chloride; a vigorous reaction ensues, and the pentacetate of gluconic acid nitrile is formed, from which hydrogen cyanide is eliminated by treatment with ammoniacal silver oxide.

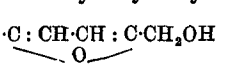
Ruff (Ber. 1898, 31, 1573) oxidises the calcium salt of gluconic acid, with hydrogen peroxide in presence of a ferrous salt (Fenton's method). The carboxyl- group is eliminated, and arabinose formed.

Neuberg (Biochem. Zeitsch. 1908, 7, 527) effects the elimination of the elements of formic acid from gluconic and similar acids by electrolysis.

Action of Acids.—Dilute acids are without action on the aldoses, but when submitted to the continued action of acids, hexoses yield lævulic acid (acetopropionic acid)

$(CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H)$

and formic acid, together with brown or black humus substances. The first product from the 2-ketohexoses is 4-hydroxymethylfurfuraldehyde



and it is to the condensation products of this aldehyde that the colour reactions of the ketoses with phenols are due. Blanksma and Ekenstein have shown that this aldehyde is also produced on heating mannose or dextrose with oxalic acid, and Fenton obtained 4-halogenmethylfurfurol from lævulose, and more slowly from the aldoses, on treatment with dry halogen hydride. The aldoses apparently undergo a 1-, 2-enolisation and conversion into 2-ketohexose.

Action of Alkalis.—Although absolutely stable in pure aqueous solution, dextrose, mannose, and fructose pass over into one another in presence of traces of alkalis in the cold. The optical rotation of a dextrose solution containing alkali, for example, slowly falls to zero. This change was observed by Lobry de Bruyn and Alberda van Ekenstein (Rec. trav. Chim. 1895, 14, 156, 204). It is due to the conversion of the sugar originally present into enol:

$CH_2(OH)\cdot[CH(OH)]_3\cdot C(OH){:}CH(OH)$

which is reconverted into all three hexoses.

Guanidine (Morrell and Bellars, Chem. Soc. Trans. 1907, 91, 1010–1033) brings about similar changes.

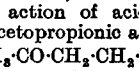
The action of alkalis on the carbohydrates is exceedingly complicated, and leads to the formation of a great variety of substances, in addition to humus compounds. The concentration of the alkali is of great importance, a larger number of products being formed when the relatively sparingly soluble lime and baryta (Kiliani) are used, than when concentrated sodium hydroxide is employed (Nef, Annalen, 1910, 376, 1).

The decomposition takes place quickly on heating, slower in the cold, with the production of acetol, acetone, lactic, acetic and formic acids, also glucinic and saccharumic acids, and other substances. With calcium hydroxide saccharin or calcium saccharinate is produced.

In addition to these substances, intermediate products are formed, more closely related to the monosaccharides, and from which these are reconstructed by the synthetic action of the alkali. It is established that hexoses break down into a molecule each of diose and aldotetrose, or into 2 molecules of glycerine aldehyde, that is, the 2 : 3 and 3 : 4-dienols decompose. The 1 : 2-dienols never break down into aldopentose and form aldehyde. Conversely, hexoses are never built up from pentoses.

Pentoses form 1 : 2-dienols, which, in the main, give aldotetroses and hydroxymethylene on decomposition; they also form 2 : 3-dienols, breaking down to diose and glycerine aldehyde.

Dextroses exclusively form 2 : 3-dienols, breaking down to 2 molecules of diose; they never give 1 : 2-dienols yielding hydroxymethylene and glycerine aldehyde. The strongly dissociated zinc hydroxide ammonia acts on the monosaccharides in the cold, producing methylglyoxaline



(Windaus, Ber. 1905, 38, 1166; 1906, 39, 3886; 1907, 40, 799).

Saccharinic acids. According to Nef (Annalen, 1910, 376, 1) there are 24 isomeric saccharinic acids, with 6 carbon atoms, namely *α*-meta-saccharinic acids (*αγδε*-tetrahydroxyhexoic acids).

$CO_2H\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2OH$

derived from the 16 aldohexoses; 4 *iso*saccharinic acids (*α*-hydroxymethyl *αγδ*-trihydroxyvaleric acids):

$CO_2H\cdot C(OH)(CH_2\cdot OH)\cdot CH_2\cdot CH(OH)\cdot CH_2(OH)$

derived from the 8 *β*-ketohexoses; 8 saccharinic acids (*α*-methyltetrahydroxyvaleric acids):

$CO_2H\cdot CMe(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2(OH)$

derived from the 8 *γ*-ketohexoses; and 4 *para*-saccharinic acids (*α*, *ω*-hydroxyethyltrihydroxybutyric acid):

$CH_2(OH)\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CH_2(OH).$

The lactones of these acids are known as saccharins. They give rise to characteristic alkaloid salts and phenylhydrazides, and possess optical activity. The saccharins are obtained by the action of lime on dextrose, maltose, or lactose.

Synthesis of Monosaccharides.—The condensation of formaldehyde under the influence of bases to carbohydrates has been the subject of repeated study. Butlerow, using milk of lime,

obtained an uncrystallisable syrup with a sweet taste, which behaved as a sugar, but was non-fermentable and optically inactive. He termed the product methylenitan. Loew improved the technique of the method by saturating a 4 p.c. solution of formaldehyde with slaked lime in the cold, and allowing it to stand. The syrupy product was termed 'formose,' and supposed by Loew to be homogeneous, but subsequently Fischer showed that on treating it with phenylhydrazine, a mixture of osazones was formed, one of which was identical with α-acrosazone. Quite recently, Nef has given reasons for believing formose (prepared by means of lead oxide) to be a mixture in approximately equal parts of isomeric hexoses and pentoses: its composition obviously depends on the alkali employed and its concentration.

Fischer and Tafel effected the condensation of acrolein dibromide by means of baryta, and showed the syrupy product to consist of two sugars, distinguished as α- and β-acrose. Subsequently, crude glycerose was made the starting-point of the synthesis. It is a mixture of glycerine aldehyde and dihydroxy acetone, both of which substances have, in after-years, been separately used as the initial material. Fenton has used glycollic aldehyde in the same manner.

A product of synthesis by all these methods is α-acrose, which is partly fermentable by yeast, and this Fischer isolated as phenylosazone, and showed to be identical with inactive *dl*-lævulose. From this by the series of reactions already given (p. 634), he obtained the natural *d*-glucose, *d*-mannose, and *d*-fructose (lævulose), as well as their optical antipodes and a number of new isomerides. The application of the methods of degradation, elsewhere described, enabled pentoses and tetroses to be synthetically prepared from these hexoses, whilst the cyanohydrin reaction made it possible to obtain monosaccharides with 7, 8, and 9 carbon atoms.

The full explanation of the synthesis of carbohydrates in the green leaves of growing plants has still to be given. It is generally supposed that formaldehyde, the first product of assimilation, undergoes polymerisation to carbohydrates, a theory advanced by Baeyer in 1870 (Ber. 3, 63). Various compounds, such as glycollic and glyceric aldehydes and dihydroxy acetone, have been suggested as intermediate stages in the polymerisation, but it has never been possible to detect any of these in the plant. Apparently the synthesis is asymmetric, hexoses of the dextro- series, and their polysaccharides being the only products of assimilation. It is supposed that the formaldehyde elements are superposed under the influence of the asymmetry of the protoplasm molecule, according to a definite plan, and are split off when six are united.

Synthesis of Disaccharides.—Though often attempted, the synthesis of disaccharides, by purely chemical means, has only been partially successful. Fischer and Armstrong have prepared a syrupy compound, probably identical with the natural sugar melibiose, by the interaction of acetochlorogalactose with sodium glucosate.

Fischer and Delbrück found that when acetobromoglucose is shaken in dry ethereal solution with silver carbonate and traces of water, the octacetyl derivative of a disaccharide is obtained. This is hydrolysed by cold barium hydroxide to a non-reducing disaccharide of the type of trehalose. The octacetyl- derivative is a mixture of isomerides, and yields isomeric disaccharides.

In the plant the disaccharides are formed from hexose by the agency of enzymes, which exercise synthetic as well as analytic functions. It is undecided whether the same enzyme can cause both synthesis and hydrolysis, or whether special enzymes alone act as synthetic agents. It is proved, however, that an enzyme effects the synthesis of a carbohydrate isomeric with that which it normally hydrolyses, the two compounds being apparently related in the same manner as the α- and β-methyl glucosides (*v.* Croft Hill, Chem. Soc. Trans. 1898, 73, 634; 1903, 83, 578; E. F. Armstrong, Proc. Roy. Soc. 1905, 76, B, 592; and monograph on Carbohydrates, 1910).

In the following pages the occurrence, preparation, properties, and derivatives of the natural, mono-, di-, tri-, and tetra-saccharides, also glycogen and inulin, are dealt with. Sucrose, the dextrins, starch, and cellulose, are described in separate articles.

Dextrose. Dextroglucose, grape sugar, starch sugar $C_6H_{12}O_6$ and $C_6H_{12}O_6,H_2O$.

Occurrence.—Reducing sugars are very widely distributed in nature, but dextrose is almost always accompanied by lævulose, the two hexoses being probably derived from sucrose. It is thus found in honey, in the juice of most fruits, and generally in vegetable tissues in small quantities. In the animal kingdom it is found in blood and in diabetic urine.

Formation.—Dextrose is formed on hydrolysing most of the known polysaccharides and glucosides, either with acids or enzymes; it is similarly formed from glycogen. Thus cellulose, starch, dextrins, the disaccharides maltose, lactose, and sucrose, all yield dextrose.

Preparation.—Dextrose is usually prepared from starch or sucrose. It can be obtained from any of the substances mentioned, but they are less suited for the preparation in quantity.

Crude commerical dextrose is purified by dissolving in 8–10 p.c. of hot water, and adding dry boiling methyl alcohol, until a cloud is produced. This solution may be decolourised by shaking with animal charcoal, and filtering. On standing, anhydrous dextrose in a pure state separates abundantly. To prepare dextrose from sucrose, the latter must first be inverted. This is best effected by treatment at a temperature not exceeding 50°, with a small quantity of invertase or of pressed yeast. After a few hours the solution is evaporated *in vacuô* to a syrup, which solidifies on standing. The mass is washed with cold ethyl alcohol (sp.gr. 0·830), and the residue dissolved in more alcohol. Dextrose crystallises on cooling.

Sulphuric acid may be used for inversion; it must be neutralised with baryta before evaporation. Soxhlet advises the use of alcoholic hydrochloric acid at 50° for 2 hours. Dextrose crystallises in a few days without neutralisation.

Properties.—Dextrose crystallises from strong (93–95 p.c.) ethyl or methyl alcohol in the anhydrous state, $C_6H_{12}O_6$, and from concentrated aqueous solutions at 30°–35°; with special

treatment, crystals of this composition may also be obtained. The crystals formed in aqueous solutions at ordinary temperatures contain a molecule of water of crystallisation, $C_6H_{12}O_6,H_2O$. The anhydride forms white crystalline crusts or powder and, when it separates from the solvent slowly, fairly well-defined glassy prisms; the hydrate crystallises in cauliflower-like masses, but with care and slow crystallisation well-defined crystals can be obtained. Both bodies dissolve easily in water, the anhydride with evolution of heat. The hydrate dissolves freely in strong ethyl or methyl alcohol, especially on the application of heat, but the anhydride is practically insoluble in these liquids.

This is Tanret's α-anhydride, m.p. 147°, $[\alpha]_D^{20}+106°$. The isomeric β-anhydride $[\alpha]_D^{20}+22{\cdot}5°$ is obtained by evaporating a dextrose solution at above 100°, and purified by treatment with 90 p.c. alcohol, in which it is sparingly soluble. γ-dextrose (the equilibrium mixture) $[\alpha]_D^{20}+52{\cdot}5°$ is obtained on precipitating a concentrated aqueous solution with alcohol. The hydrate begins to melt at 80°, complete fusion is not effected till 100°, when all the water is expelled.

An aqueous solution of dextrose containing 10 grams anhydrous dextrose in 100 c.c. of solution at 15·5°, has a sp.gr. 1·0385. Its solutions are optically active, *i.e.* possess the power of rotating the plane of polarisation of a ray of polarised light. The rotation is right-handed. Hesse (Annalen, 176, 106) and Tollens (Ber. 17, 2234) have carefully determined this constant, and the latter's results are expressed by the formula

$$[\alpha]_D = 52{\cdot}5°+0{\cdot}018796P+0{\cdot}00051683P^2$$

for the dry sugar, and

$$[\alpha]_D = 47{\cdot}73°+0{\cdot}015534P+0{\cdot}0003883P^2$$

for the hydrate $C_6H_{12}O_6,H_2O$, in which P = the percentage of anhydride and hydrate in solution. In dealing with solutions containing 10 p.c. dry sugar, the factors $[\alpha]_D = 52{\cdot}7°$ and $[\alpha]_j = 58{\cdot}3°$ may be used. The optical activity of dextrose solution is not materially affected by temperature. The activity is nearly twice as great in freshly prepared solution, diminution taking place slowly in cold, but rapidly in boiling solutions, until the constant value is arrived at. It is only crystallised dextrose that exhibits this property of bi-rotation, as it is called, dextrose fused and allowed to solidify does not show it (Hesse, Annalen, 176, 113). The solution of dextrose in strong alcohol retains the power of bi-rotation. (For the explanation of bi-rotation, *see* p. 632.)

When dextrose is heated to 170°, the elements of a molecule of water are eliminated, **dextrosan** (glycosan) $C_6H_{10}O_5$ being produced. If the temperature is increased, that body is caramelised and charred. Dextrosan is again converted into dextrose by digestion with water or dilute acids. It is a hygroscopic, dextro-rotatory, non-fermentable substance. If the temperature is raised to 200°, and maintained at that point for a little time, gas, water, and volatile acids are given off, and if the heating is continued without being increased until these products cease to be evolved, the brownish-black residue (caramelised mass) becomes gradually solid. This substance is soluble in water, completely if the temperature was not too high, and constitutes the colouring matter used in wine, beer, cookery, &c. Should the heat be further continued so that the body is destructively distilled, carbon mon- and di-oxide, and methane are evolved, aldehyde, furfuraldehyde, acetone, propionic, acetic, and formic acids, furane and furfurol distil over, and a black carbonaceous mass is left.

The action of alkalis and of acids on dextrose has been discussed elsewhere. When reduced by sodium amalgam, the main product (35–40 p.c.) is sorbitol; some quantity of mannitol is also formed in alkaline, but not in neutral or acid solution. It is derived from the mannose produced by the action of alkali on dextrose.

Oxygen has no action on dextrose in neutral or acid solutions, but alkaline solutions absorb the gas. Ozone oxidises it to formic acid, saccharic acid, &c., being produced. Strong nitric acid converts dextrose into saccharic acid, and finally into oxalic, carbonic, and formic acids. Treated with chlorine or bromine in the presence of water, the resulting product yields gluconic acid when submitted to the action of silver oxide.

Dextrose in alkaline solutions reduces the oxides of gold, platinum, silver, mercury, bismuth, lead, copper, iron, manganese, &c.; in the case of gold, platinum, silver, and mercury, the reduction is complete, the metal being formed; in the other cases lower oxides are produced. Ferrocyanide of potassium, indigo, picric acid, litmus, and such substances are also reduced by dextrose in alkaline solution. The products from the dextrose are not the same in all cases, but they consist chiefly of carbonic, formic, oxalic, and glycollic acids, other products being also formed.

Nearly all the true yeasts (*Saccharomyces membranæfaciens* is an exception), a great number of torulæ, moulds, and other organisms ferment dextrose, yielding carbon dioxide and alcohol as the chief products. Glycerol, succinic acid, and other bodies (fusel oil) are formed at the same time, the proportions of these bodies varying materially with the organisms and the conditions under which the growth takes place. The work of Ehrlich suggests that most of these by-products are derived from amino-acids, produced from the yeast and not from dextrose (*v.* FERMENTATION).

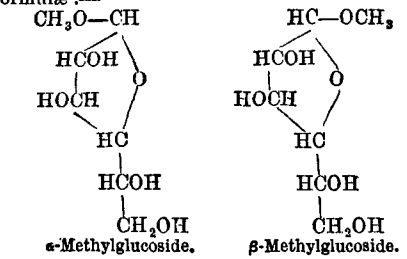
Pressed yeast-juice, zymase, which contains no living protoplasm, also ferments dextrose.

In the presence of growing bacteria of various species, dextrose yields many products, one species converts it into lactic acid, another into butyric acid, another into cellulose, the so-called slimy fermentation, and so on. Other organisms oxidise dextrose (*v.* FERMENTATION).

Dextrose combines with sodium chloride, bromide, and iodide, forming well-defined crystalline compounds; these decompose in aqueous solution. Compounds with bases are indefinite in character, and unstable. Sodium and potassium dextrosate $C_6H_{11}MO_6$ are obtained on adding sodium or potassium ethoxide to an alcoholic solution of dextrose. Several

calcium dextrosates are described containing varying proportions of dextrose, lime, and water. Dextrose is not precipitated with lead acetate, but basic lead salts are obtained in presence of ammonia.

The methylglucosides. These are of importance, as types both of glucosides generally, and of the two isomeric series of dextrose derivatives. They are regarded as stereoisomeric γ-oxides, and have the following structural formulæ :—



α-Methylglucoside. β-Methylglucoside.

α-Methylglucoside crystallises in long needles, m.p. 165° $[\alpha]_D$ +157°; β-methylglucoside forms rectangular prisms, m.p. 104° $[\alpha]_D$ −33°.

They are hydrolysed by warm mineral acids to methyl alcohol and dextrose, the β-isomeride being attacked 1·8 times as rapidly as the α-isomeride. Each glucoside requires its own particular enzyme to hydrolyse it. α-Methylglucoside is hydrolysed by maltase alone; β-methylglucoside only by emulsin. They are used as test materials in studying enzyme action.

The isomerides are both formed when dextrose is heated with methyl alcohol containing hydrogen chloride.

To obtain α-methylglucoside, 1 part of dextrose is heated with 4 parts methyl alcohol containing 0·25 p.c. hydrogen chloride, for 50 hours in an autoclave. The solution deposits crystals of the glucoside on evaporation, and the mother liquors, after further heating, give a second and third crystallisation, as the β-isomeride present is converted into the α- by the acid. A yield of 80 p.c. or more is obtained.

To obtain β-methylglucoside, solid anhydrous glucose is dissolved in methyl alcohol, nearly saturated with dry hydrogen chloride, at room temperature. As soon as etherification is complete, as witnessed by the absence of reducing power, the solution is neutralised and evaporated, and a mixture of α- and β-isomerides obtained in about equal quantities. The α- is partly separated by crystallisation from strong alcohol. The residue is dissolved in water, and fermented by a pure culture yeast. The α-methylglucoside is hydrolysed, and the dextrose fermented; the β-methylglucoside remains untouched, and is recovered and purified.

The other carbohydrates form analogous methylglucosides, and similar compounds are obtained with ethyl alcohol. (For other artificial glucosides, *v.* GLUCOSIDES.)

A very large number of dextrose compounds have been prepared, in some of which the aldehydic hydroxyl is concerned, whilst others, *e.g.* the acetates, involve all five hydroxyls. As already stated, in most cases two isomerides derived from α- and β-dextrose have been prepared. Few of these compounds are really characteristic of dextrose, and it must suffice in the space at disposal to indicate the properties of some of them in tabular form.

Compound	Appearance	M.p.
Pentanitrate	amorphous	—
α-pentacetate	colourless needles	112°–113°
β-pentacetate	granular crystals	134°
α-acetochlorodextrose	long needles	63°–64°
β-acetochlorodextrose	stellate aggregates	73°–74°
α-acetobromodextrose	prisms	79°–80°
β-acetobromodextrose	lustrous needles	88°–89°
α-acetonitrodextrose	needles	92°
β-acetonitrodextrose	lustrous rhombic prisms	150°–151°
Pentabenzoate	needles	179°
Trimethyldextrose	colourless syrup	—
Tetramethyldextrose	needles	81°–83°
Pentamethyldextrose	stellate crystals	42°–43°
Dextroseethylmercaptal	colourless matted needles	127°–128°
α-chloralose	bunches of needles	186°
β-chloralose	fatty plates	230°
Dextrose diacetone	needles	107°–109°
Dextrose ureide	rhombic plates and needles	207°
Semicarbazone	needles	175°
Thiosemicarbazone	rhombic plates	204°
Anilide	needles	147°
Oxime	needles	137°
Phenylhydrazone	needles or plates / needles	144°–146° / 115°–116°
Bromophenylhydrazone	needles	147°
Methylphenylhydrazone	colourless plates	130°
α-amylphenylhydrazone	light brown needles	128°
α-allylphenylhydrazone	light yellow needles	155°
α-benzylphenylhydrazone	light yellow needles	165°
Diphenylhydrazone	colourless oblique prisms	161°
β-naphthylhydrazone	brown needles	95°
Phenylosazone	aggregates of yellow needles	206°
p-bromophenylosazone	yellow needles	222°
Nitrophenylosazone	reddish needles	257°
Dextrose-*o*-diaminobenzene	colourless lustrous needles	—
Didextrose-*o*-diaminobenzene	slender colourless needles	—
Dextrose-γ-diaminobenzoic acid	lustrous silver plates	243°

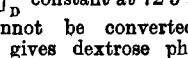
d-Glucosamine (Chitosamine) or aminodextrose has the formula

$$CH_2(OH)\cdot[CH(OH)]_3\cdot CHNH_2\cdot CHO.$$

It is obtained by boiling the shells of lobsters, particularly the claws, with concentrated hydrochloric acid, when the hydrochloride results The shells of lobsters consist of carbonate of lime and chitin. Chitin is a constituent of various invertebrate skeletal structures, and of the cell walls of fungi; it is considered by Irvine to contain acetylamino-dextrose and amino-dextrose residues in the proportion of 3 to 1 $(C_{30}H_{50}O_{19}N_4)n$. It is prepared from the hydrochloride by decomposing it with diethylamine (Breuer, Ber. 1898, 31, 2193) or sodium methoxide (Lobry de Bruyn, *ibid.* 1898, 31, 2476). Fischer and Leuchs (Ber. 1903, 36, 24) effected the synthesis by the combination of *d*-arabinose and ammonium cyanide to *d*-glucosaminic acid, the lactone of which was reduced to *d*-glucosamine. Glucosamine forms a colourless crystalline powder, or long needles; m.p. 115° $[\alpha]_D$ +48°. The aqueous solution reacts alkaline, but is stable. It is not fermentable. The pentacetate exists in two forms, needles, m.p. 183·5° and 133° respectively; the former is optically inactive, the latter has $[\alpha]_D$ +86·5°. The oxime forms prisms, m.p. 127°. Two modifications of the hydrochloride are known: glistening monoclinic crystals $[\alpha]_D^{20}$ + 100°,

falling to +72·5° on standing, and hexagonal needles $[\alpha]_D^{20}$ constant at 72·5°.

It cannot be converted into dextrose, though it gives dextrose phenylosazone when heated with phenylhydrazine. By the action of nitrous acid, a compound, $C_6H_{10}O_5$, is formed, which was at one time regarded as a carbohydrate, and termed chitose, but was shown by Fischer and Andreae (Ber. 36, 2587) to be a hydrated furfurane derivative



Chitose forms an oxime and phenylhydrazone and is oxidised by bromine to chitonic acid. Glucosamine was formerly regarded as a derivative of chitose, and termed chitosamine.

An isomeride of glucosamine is *iso*glucosamine $CH_2(OH)\cdot[CH\cdot(OH)]_3\cdot CO\cdot CH_2\cdot NH_2$, which Fischer obtained by reducing phenylglucosazone with zinc-dust, and which is converted by the action of nitrous acid into lævulose.

Manufacture of commercial dextrose—i.e. dextro-glucose, glucose, saccharum, saccharine, &c.—These products, varying much in character and composition, are all prepared by the action of acids on starch or starchy substances, such as rice, maize, &c., and when these latter are the raw material, it has been proposed to employ the combined action of diastase and acids. When starch is acted upon by dilute acids, it is dissolved, dextrins and maltose being produced. These bodies, by the further action of the acid, yield dextrose; this itself does not resist the action of acids, so that during the process of conversion, a portion of it is attacked, with the production of substances imperfectly studied (*v.* ISOMALTOSE, p. 652).

The phases of the action of dilute acids on starch are easily followed. After heating has been continued for a short time, a portion of the solution cooled ceases to give a blue colouration with iodine; this indicates absence of starch; in the place of this a reddish-brown colouration is produced, this indicates the presence of α-dextrin. After a time this disappears, and at length the solution ceases to give a precipitate, when to a portion of it twice its bulk of alcohol (sp.gr. 0·820) is added, or when to a portion from which the sulphuric acid has been separated by baryta-ammoniacal lead acetate is added. This establishes the absence, not of maltose, but only of dextrin. For syrup the boiling is stopped as soon as the iodine test gives a port-wine colour; for solid dextrose it is continued till alcohol causes no precipitate. The processes involved in the manufacture may be conveniently arranged as follows:—

(*a*) The conversion.
(*b*) The neutralisation.
(*c*) The filtration.
(*d*) The decolourisation.
(*e*) The concentration.
(*f*) The purification.

(*a*) *The conversion.*—In this country the materials chiefly employed in the manufacture of commercial dextrose are sago, maize, and rice starch, finely ground rice itself, as well as granulated maize and rice being at times used. Potato starch is also used in Germany. In America green-maize starch is the chief material; hence the term 'corn sugar.' The acid usually employed in Europe is sulphuric; hydrochloric acid is generally used in America; and nitric acid as well as a mixture of nitric and sulphuric acids have been recommended. The use of sulphurous and orthophosphoric acids has also been advocated. The proportions of material, water, and acid generally employed in the case of sulphuric acid are 100 : 250 : 5, and when green starch, *i.e.* undried purified starch, is used, 1½ parts are taken instead of 1 part dry starch. When pressure converters are used, the acid can be reduced to 0·5 p.c.

Formerly open converters made of wood, lined with lead and provided with steam coils of lead and stirring gear, were used, but these are now abandoned nearly everywhere for closed converters. These are made of cast iron, copper, or gun metal, and are worked at a pressure of 30 lbs. of steam.

The operations involved in the manufacture, whatever converter is used, are as follows: Half the sulphuric acid is mixed with half the water in a separate vat constructed as the converter, with or without coil, and at such a temperature that the heat of the dilute acid will be less than the gelatinising point of the starch of the material employed. This vat is furnished with stirring gear, and placed under a hopper, in which is stored the starch or starchy substance. When the dilute acid is at the right temperature, the material is allowed to flow into it, the stirring gear being kept in motion; a milk of starch in dilute acid is thus obtained. Meanwhile the remaining half of the acid and water are introduced into the converter, and heated to boiling, then the starch milk is run in at such a rate that the temperature does not fall far below boiling, and the introduction should be effected as rapidly as possible.

The time required for conversion depends on the rate of introduction of the starch milk, and on the pressure employed, &c. For corn syrup an average time from the commencement of the starch introduction to the discharge is a little over an hour, for solid sugar about 1½ hours is required. When converted, the liquid is blown into the neutralising vats.

(*b*) *The neutralisation.*—Finely-ground chalk is used to neutralise the acid employed in the conversion. The chalk is converted into a milk with water, and gradually introduced into the converted liquid. About 12 lbs. of powdered chalk are taken for every 10 lbs. sulphuric acid employed; this is more than the theoretical quantity, but it is found to answer in practice, owing, no doubt, to the insolubility of a portion of the chalk. The neutralised liquid is kept stirred for some time, and is then allowed to rest. It is found best to allow it to cool and settle gradually, and then draw off the clear portion; but where vat room is a consideration, the neutralised liquid is run immediately to the filter presses (*v.* FILTRATION).

(*c*) (*d*) The clear filtered solution is passed through bone-char filters of the same construction as those described under SUGAR. Sulphurous acid is sometimes used in bleaching the product.

(*e*) *Concentration.*—This operation is effected in vacuum pans (*v.* SUGAR), and is considered complete when the syrup contains about 82 p.c. solid matter, *i.e.* reaches a sp.gr. of 1·50. It is

then run into moulds, usually cone-shaped vessels, in which, on standing and cooling, it solidifies after a short time. This is hastened by the introduction of some previously solidified sugar. The solidified mass extracted from the mould by a short immersion in hot water is broken into irregular lumps, in which form it appears in the market. The colour of the commercial parcels varies from pure white to dark-brown; this depends on the character of the material employed (the purity and variety of the starch), on the mode of conversion, and the extent to which the decolourisation was carried. The composition is also very variable, but the constituents in all are the same, viz. dextrose, maltose, dextrin, unfermentable organic bodies, and ash. Very few samples contain dextrin, some few maltose, and the proportion of unfermentable bodies varies very much, being sometimes as high as 15 p.c. The syrups, which are used in confectionary, contain a large percentage of dextrin and maltose.

In the United States the conversion is carried out by stirring the green-corn starch, made in the same factory, with a large body of water, and subjecting this mixture to a high heat under pressure, the process being a hydrolytic one. A small amount of pure hydrochloric acid is added to facilitate the catalytic action. The conversion is performed in large vessels 6 feet in diameter, and about 20 feet high, made of hammered copper 1 inch in thickness.

After the required conversion, the traces of acid are neutralised with soda ash, the mixture being left very slightly acid to litmus, and excess of alkali being very carefully avoided, as the least trace colours the liquid. In the case of glucose syrup, conversion is complete in less than 10 minutes; conversion into anhydrous dextrose takes considerably longer. The converted starch, now an almost white liquor, is run from the neutralisers through filter presses, to remove the dissolved gluten, &c., which is precipitated during neutralising, and then through an evaporator, which reduces the gravity to 30°B. It is then run sucessively over three bone-char filters, each 10 feet in diameter and 24 feet high, and containing 70,000 lbs. of bone-char each. The liquors receive a much greater amount of bone-char treatment than is the custom in sugar refineries, passing, in all, over 72 feet. The remaining traces of acid are completely neutralised, and the liquid has a brilliant crystal-white appearance. The bone-char is revivified after each bath. The liquor is concentrated in vacuum pans to the required density 42°–45°B., and crystallises on cooling. (A full account of the American industry of corn products is given by Wagner (J. Soc. Chem. Ind. 1909, 28, 343).)

The average composition of these products is as follows :—

—	Corn syrup	70 sugar	80 sugar	Anhydrous sugar
	P.c.	P.c.	P.c.	P.c.
Water .	19·0	19·7	11·2	4·0
Dextrose .	38·5	70·2	79·9	94·6
Dextrin .	42·0	9·3	8·0	0·7
Ash. .	0·5	0·8	0·9	0·7

The ash consists principally of chlorides.

(*f*) *Purification.*—Behr (Eng. Pat. 9797, 1884; 1767, 1885) manufactures pure commercial crystalline anhydrous dextrose by adding crystals of dextrose to a solution concentrated to 85 p.c., and allowing the mixture to stand at about 35°. After a short time an abundant crop of crystals separates, and by treatment in a centrifugal machine, the uncrystallised syrup is removed (*v.* SUGAR).

In the older process of Soxhlet, the concentrated syrup was dissolved in about an equal weight of boiling methyl alcohol, and allowed to stand. The crystals were drained, and the loaves washed with methyl alcohol, which was recovered from the loaves and mother liquors by distillation in a vacuum.

Dextrose from Cellulose.—Cellulose is disintegrated by boiling with acids only with great difficulty, and at high temperatures, with the formation of dextrose, and the process cannot compete industrially with the preparation from starch. Numerous attempts have been made to obtain dextrose from wood cellulose, with the industrial objective of the manufacture of alcohol.

Simonsen (Zeitsch. angew. Chem. 1898, 195, 219, 962, 1007) found the most favourable conditions for the conversion of 40 grams of cellulose to be a digestion for 2 hours at 6–8 atmospheres, with 1000 c.c. of 0·5 p.c. sulphuric acid. 45 p.c. of reducing sugar was obtained, but, according to Körner (*ibid.* 1908, 2353), this is not all fermentable dextrose.

Ekström (Fr. Pat. 380358, July 29, 1907) treats sawdust with 95 p.c. sulphuric acid at the ordinary temperature for 20 minutes, dilutes to 1 p.c. free acid, and heats from 1 to 5 hours under a pressure of 3–8 atmospheres; 55–57 p.c. conversion is claimed.

Ewen and Tomlinson (U.S. Pat. 938308, Oct. 26, 1909) heat sawdust with a minimum of 5 p.c. acid to a temperature between 135° and 162°. The use of 2–6 p.c. hydrofluoric acid has also been suggested (Orlowski, Fr. Pat. 405187, July 17, 1909).

d-**Mannose** $C_6H_{12}O_6$ occurs in nature in the form of anhydride-like condensation products, known as mannosans. It is best prepared from the vegetable ivory nut (*steinnuss*) which is used in Berlin and elsewhere for the manufacture of buttons and collar studs. The waste turnings are hydrolysed to mannose by boiling for 6 hours with 2 parts of hydrochloric acid. It was originally obtained by Fischer and Hirschberger by oxidising mannitol with nitric acid. Mannose is characterised by forming an insoluble yellow phenylhydrazone, m.p. 186°–188°, and use is made of this compound in isolating it from solution. The hydrazone is subsequently decomposed with benzaldehyde, or better, formaldehyde, and the resulting solution concentrated *in vacuo* till the sugar crystallises.

Mannose separates in colourless rhombic crystals [$a : b : c = 0{\cdot}319 : 1 : 0{\cdot}826$] of sweet taste, m.p. 132°. 100 c.c. of the saturated aqueous solution at 17·5° contain 24·8 grams; in absolute alcohol it is almost insoluble. It shows muta-rotation, the equilibrium value being $[\alpha]+14{\cdot}5°$.

It is very similar to dextrose in all its properties, yielding the same phenylosazone. It is fermented by all yeasts which attack dextrose

and lævulose. Bromine oxidises it to mannonic acid; sodium amalgam reduces it to mannitol. α-Methyl mannoside has m.p. 190°, $[\alpha]_D^{20}$ +80°. The oxime crystallises in colourless needles, m.p. 167°–180°. Like the phenylhydrazone, the substituted hydrazones are all sparingly soluble.

Caroubinose, a carbohydrate isolated from the seeds of the carob bean, is identical with mannose.

d-Galactose $C_6H_{12}O_6$. Milk sugar, when hydrolysed by means of acids or enzymes, yields dextrose and galactose in equal proportions. On a commercial scale, sulphuric acid is used to effect hydrolysis under pressure at 105°, after which the solution is neutralised and concentrated until an amount which contained 500 grams of milk sugar weighs 640 grams. The syrup is set aside with a few crystals of galactose, and, after some days, the crystalline mass is washed with 80 p.c. alcohol, and the galactose purified by recrystallisation from aqueous alcohol. Even the very best commercial galactose contains minute quantities of dextrose: to remove this it must be treated with a pure culture of some yeast, such as *S. Ludwigii*, which ferments dextrose, but not galactose.

Galactose is a constituent of raffinose and stachyose, and is widely distributed in the polymeric form, galactan, particularly in gums and seaweeds. It occurs in a few glucosides. It is a colourless crystalline powder, m.p. 162°, less soluble than dextrose, and has the same general properties as dextrose. The most characteristic behaviour is the formation of mucic acid on oxidation with nitric acid.

Galactose exhibits muta-rotation; the α-isomeride has $[\alpha]_D^{20}$ about +140°, the β-modification about +53°. The equilibrium value is $[\alpha]_D^{20}$ +81°. The influence of concentration and temperature on this value is expressed by the equation

$$[\alpha]_D = 83{\cdot}883 + 0{\cdot}0785p - 0{\cdot}209t,$$

where p and t denote concentration and temperature respectively.

Galactose derivatives are prepared similarly to the corresponding dextrose compounds. The α-pentanitrate (Will and Lenze, Ber. 31, 68) forms needles, m.p. 115°–116°; the β-isomeride has m.p. 72°–73°; the β-pentacetate has m.p. 142°; α-methylgalactoside has m.p. 111°–112°, $[\alpha]_D^{20}$ +179·3°, and crystallises in transparent doubly refractive needles; the β-isomeride forms needles, m.p. 173°–176°, $[\alpha]_D^{20}$ +2·6°; the phenylhydrazone has m.p. 158°, the phenylosazone when quickly heated melts at 193°–194°.

Some yeasts ferment galactose, but not all those which ferment dextrose and lævulose. It is apparently possible to grow a yeast in presence of galactose and dextrose, until it acquires the power of fermenting galactose. Galactose is identical with the sugar cerebrose, isolated from the brain by Thudichum, where it is a constituent of the cerebrosides, phrenosin and kerasin.

Lævulose or d-Fructose $C_6H_{12}O_6$ is a ketohexose or ketose sugar. It is found together with dextrose in honey and in many fruits, and, combined with dextrose, it occurs in sucrose, raffinose, stachyose, &c. Inulin, found in dahlia tubers is completely converted into fructose on hydrolysis. It has not so far been produced by the hydrolysis of any glucoside.

It is termed *d*-fructose, in spite of the lævo-rotation, to indicate that it belongs to the *d*-mannitol series.

After prolonged heating at 165°–170°, cane sugar becomes converted into a mixture of lævulosan ($C_6H_{10}O_5$) and dextrose, without change of weight. On fermenting the aqueous solution of the mass with yeast, the dextrose is decomposed, while the lævulosan remains unchanged, and may afterwards be converted into lævulose by treatment with dilute acids.

Preparation.—It is best prepared from inulin. 100 grams of inulin with 1 p.c. ash are heated with 250 c.c. water and 0·5 gram hydrochloric acid for half an hour in a boiling water-bath, neutralised with 1·5 grams sodium carbonate evaporated on the water-bath at 60°, and finally over sulphuric acid *in vacuô* to a thick syrup. This is extracted with absolute alcohol, put aside for 24 hours, the solution poured off clear, and inoculated. Complete crystallisation of the lævulose is obtained in 3 days, and it is quite pure after one more crystallisation.

Inulin may also be hydrolysed with 0·5 vol. p.c. oxalic acid.

(For the preparation from Jerusalem artichokes, *see* U.S. Pat. 879422, Feb. 18, 1908.)

To obtain lævulose from sucrose, the latter is first inverted by means of mineral acids or invertase, and the acid removed by neutralisation with baryta or silver oxide. The invert sugar resulting contains both dextrose and lævulose, which may be separated as follows: 6 grams of finely powdered slaked lime is added to every 100 c.c. of a neutral ice-cold 10 p.c. solution of invert sugar, and the solution, which at first sight is merely milky, is agitated, the vessel being preferably immersed in ice-cold water until it acquires a creamy consistency. The mass, which consists of the difficultly soluble calcium lævulosate $CaO{\cdot}C_6H_{12}O_6{\cdot}H_2O$, together with the easily soluble calcium dextrosate, is filtered through linen, and strongly pressed to remove the greater part of the liquid, and is suspended in water and decomposed by addition of oxalic acid or by passage of carbonic acid gas. The filtered solution is evaporated *in vacuô* over sulphuric acid, with production of anhydrous lævulose. Calcium lævulosate dissolves in 137 parts of water at 15°, and is almost insoluble at 0°.

Lævulose, when pure, crystallises from alcohol, and even from aqueous solution in needles, also in crusts of transparent prisms, which are not hygroscopic. It has m.p. 95°, $D^{17·5}$ 1·669. It is very soluble in water, almost insoluble in cold absolute alcohol. It is much sweeter than dextrose, and somewhat sweeter than sucrose. It exhibits muta-rotation, and, no doubt, exists in solution as an equilibrated mixture of stereoisomeric γ-oxide forms. The initial rotation $[\alpha]_D^{20}$ −104° falls to $[\alpha]_D^{20}$ −92° (Parkus and Tollens, Annalen, 257, 160). The specific rotatory power is very considerably influenced by changes of temperature and concentration, which cause an alteration in

the proportions of the isomerides in the equilibrium mixture. The rotatory power usually taken is $[\alpha]_D^{15}$ −93·8°. It falls 0·6385° for each degree centigrade of increase in temperature, and at 87·3° is equal but opposite to that of dextrose. This property is taken advantage of in determining its proportion in presence of other sugars, the rotation being observed at two different temperatures.

According to Soxhlet, the relative reducing powers of lævulose and dextrose on Fehling's solution, in 1 p.c. solution, are 475:513; but Allihn finds that if the solutions be boiled for 30 minutes (instead of for 2 minutes, as in Soxhlet's experiments), their reducing powers are identical. On Knapp's mercurial solution their action is the same, but on Sachsse's mercurial solution their actions are 100 (lævulose) and 148·6 respectively.

Oxidation converts lævulose into acids with fewer carbon atoms, glycollic and trihydroxybutyric. On reduction with sodium amalgam, mannitol and sorbitol are formed. Acids attack it far more readily than dextrose with the production of lævulic and formic acids; alkalis somewhat less readily. Heating concentrated solutions with oxalic acid forms 4-hydroxymethylfurfurol, whilst it interacts with hydrogen bromide in ethereal solution, forming 4-bromomethylfurfurol $\begin{matrix}CH : C(CH_2Br)\\ CH : C(CHO)\end{matrix}\!\!>\!O$ (Fenton and Gostling, Chem. Soc. Trans. 1899, 75, 423; 1901, 79, 361).

It is fermented by all yeasts which attack dextrose.

By the action of methyl alcohol and hydrogen chloride (0·5 p.c.) at 35°, a syrup is obtained which probably represents a mixture of methyl fructosides. It is partially hydrolysed by yeast extract.

Fructose diacetone $C_{12}H_{20}O_6$, prepared in a similar manner from acetone, forms needles, m.p. 119°–120° $[\alpha]_D$ −161°. An isomeride has m.p. 97° $[\alpha]_D$ −33·7°.

The osazones of lævulose are identical with those of dextrose. Lævulose is more easily oxidised by disubstituted phenylhydrazines, and forms a characteristic osazone with methylphenylhydrazine, long yellow needles, m.p. 158°–160°.

To prepare this, 4 grams of methylphenylhydrazine are added to 1·8 grams lævulose, in 10 c.c. water, and enough alcohol to make a clear solution further 2 c.c. of acetic acid are added, and the mixture heated 5–10 minutes at most on the water-bath. It is then covered and allowed to stand. Within 2 hours red crystals are obtained, which may be recrystallised from 10 p.c. alcohol.

Sorbose (Sorbinose) $C_6H_{12}O_6$ is the ketohexose obtained from the juice of the mountain-ash berries, which has been exposed to the air and allowed to ferment. The juice contains sorbitol; this is oxidised by *bacterium xylinum* to sorbose.

The juices are evaporated to 1·05 sp.gr., allowed to stand some days till the sugar is fermented, and the clear liquid poured into flat dishes and inoculated with an active culture of *B-xylinum* (Bertrand, Ann. Chim. Phys. 1904, [viii.] 3, 181). This is left at 30° till the reduction is a maximum, clarified with lead acetate, excess of lead precipitated as sulphate, and the neutral filtrate concentrated *in vacuô*. When pure sorbitol is available, 100 grams are dissolved in 500 c.c. water, some nutrient solution for the bacterium added, and the fermentation carried out as above.

Sorbose forms rhombic crystals of a sweet taste, m.p. 154°; it reduces Fehling's solution, and generally behaves as lævulose, but yields sorbitol on reduction. It is not fermentable by yeasts. It is lævo-rotatory, having $[\alpha]_D$ −42°.

Sorbose phenylosazone is similar to the dextrose compound, but has m.p. 164°.

The properties are in agreement with the structural formula:

$$\begin{matrix}&HO&H&OH&\\ CH_2OH\cdot CO\cdot C&\cdot&C&\cdot&CH_2OH\\ &H&OH&H&\end{matrix}$$

Methyl sorbinoside crystallises in transparent thick plates, m.p. 120°–122° (Fischer, Ber. 28, 1159).

Pentoses $C_5H_{10}O_5$.

Only two pentoses occur naturally. These are widely distributed in plants, where they are present in the skeletal structure, and do not, like the hexoses, serve as food products. Pentoses also appear to be a constituent of many of the tissues of the animal body, and are sometimes found in urine. Both the natural pentoses, *l*-arabinose and *l*-xylose, belong to the *lævo*- series. Dextrose (*dextro*-glucose), when degraded by the methods of Ruff or Wohl, gives rise to the isomeric *d*-arabinose. However, the natural pentoses are very closely related to the natural hexoses. For example, the space arrangement of the groups attached to the upper four carbon atoms, is the same in *d*-glucose as it is in *l*-xylose:

l-Xylose.	*d*-Glucose.	*d*-Arabinose.
CHO	CHO	CHO
HCOH	HCOH	HOCH
HOCH	HOCH	HCOH
HCOH	HCOH	HCOH
CH_2OH	CH_2OH	CH_2OH

A similar relationship exists between galactose and arabinose, which occur together in many gums, whilst some polysaccharides yield both xylose and glucose on hydrolysis. The pentoses do not occur as such, but in the form of condensation products of high molecular weight, termed 'pentosans' (araban or xylan). These are comparable with the hexose condensation products, starch and cellulose; as a rule, the pentosans contain both C_5 and C_6 carbohydrates.

The mechanism of the formation of pentoses in the plant is not yet clear. Some authorities consider they are derived by oxidation from the hexoses; others advocate the view that they are directly formed in the cell, like the hexoses, but independently of these. Such a transformation as that from dextrose to *l*-xylose has not been effected in the laboratory: the chemical degradation of dextrose by oxidation leads to *d*-arabinose.

The pentoses show all the general chemical properties of the hexoses. Biochemically, they are different, being not fermentable by yeasts, whilst their glucosidic derivatives (*e.g.* the methyl arabinosides and xylosides) are not hydrolysed by any of the better-known plant enzymes. They are attacked by a number of bacteria. Characteristic of the pentoses is the formation of furfurol on distillation with hydrochloric acid. They, therefore, show colour reactions with orcinol and phloroglucinol. Equal parts of concentrated hydrochloric acid and water are taken, together with the pentose and a little orcinol or phloroglucinol, and the mixture warmed in the water-bath. With orcinol the solution becomes red, then violet, and finally blue or blue-green, with the separation of a precipitate which dissolves in amyl alcohol, giving a blue-green solution; this shows an absorption band between C and D. With phloroglucinol the solution becomes cherry-red, and a precipitate is formed, giving a red solution in amyl alcohol, with an absorption band between D and E.

***l*-Arabinose** $C_5H_{10}O_5$ is obtained by hydrolysis of most gums, particularly gum arabic and cherry gum.

Preparation.—A solution of gum arabic, or allied gum (dextro-rotatory, and yielding little mucic acid by the action of nitric acid, by preference), containing 30–40 grams of the gum, and 2–3 c.c. sulphuric acid in 100 c.c., is boiled for 7–12 minutes, cooled, the acid neutralised with calcium or barium hydroxide or carbonate and alcohol, sp.gr. 0·83 added as long as a precipitate is produced. This precipitate soon settles, leaving the alcoholic solution clear. On distilling off the alcohol and evaporating to a syrup, arabinose crystallises out. The substance is obtained in well-defined rhombic prisms, with monoclinic termination, by recrystallising from water. With some gums the digestion of the acid solution can be continued for 2 hours with increased yield of arabinose, and without impairing the purity of the product. The crystals are anhydrous; m.p. 160°.

Arabinose has $[\alpha]_D$ +104° to +105°, the activity increasing with the strength of the solution, and decreasing as the temperature at which it is observed is raised.

It exhibits muta-rotation, *α*-arabinose having the initial rotatory power $[\alpha]_D$ +175°, decreasing to +104°. *β*-Arabinose has not been isolated. Accordingly, like dextrose, it has a *γ*-oxidic structure.

The heat of combustion is 558 cals.

Arabinose reduces Fehling's solution, the amounts of copper oxide produced by equivalent weights of arabinose and dextrose being as 111 : 100.

Bromine oxidises it to *l*-arabonic acid $C_5H_{10}O_6$, which crystallises as the lactone $C_5H_8O_5$, m.p. 95°–98°, $[\alpha]_D$ −73·9°. Nitric acid forms oxalic acid as the final product, but in dilute solution, firstly arabonic acid, and secondly *l*-trihydroxyglutaric acid, m.p. 127°, are formed. On reduction, amongst other products, *l*-arabitol, m.p. 102°, is formed, which is optically inactive, but becomes lævo-rotatory in presence of borax.

Arabinose forms an additive compound with hydrogen cyanide, which is hydrolysed to arabinose carboxylic acid. This is, in reality, a mixture of two acids, of which the lactones on reduction give rise to *l*-glucose and *l*-mannose.

The diphenylhydrazone, m.p. 218°, is almost insoluble. The other hydrazones have the following melting-points: phenyl, 151°; *p*-bromophenyl, 150°; *α*-methylphenyl, 161°; *α*-ethylphenyl, 153°; *α*-amylphenyl, 120°; *α*-allylphenyl, 145°; *α*-benzoylphenyl, 170°; *β*-naphthyl, 141°. Arabinose phenylosazone, m.p. 160°, is prepared similarly to the dextrose compound. It is slightly more soluble, and, when boiled with benzaldehyde, arabinosone is formed. The *p*-bromophenylosazone has m.p. 196°–200°.

Arabinose forms crystallisable compounds, with the aromatic diamines and diamino-acids.

***l*-Xylose** is obtained by the hydrolysis of wood gum (xylan) extracted from wood by dilute soda solution.

According to Bertrand (Bull. Soc. chim. [3] 5, 554), it may be obtained from wheat or oat straw by first extracting the straw with tepid water, and then boiling it for several hours with dilute (1–2 p.c.) sulphuric acid. The liquor, after removal of the sulphuric acid by baryta, is concentrated on the water-bath and treated with alcohol; this extracts the xylose, which forms a syrup on evaporation of the alcohol, solidifying on the addition of a crystal of xylose. The yield is about 2 p.c. from wheat straw, and 4 p.c. from oat straw.

Another convenient source are oat hulls, which are cleaned by soaking in dilute ammonia, washed and hydrolysed with sulphuric acid. Xylose crystallises in orthorhombic prisms, m.p. 144°–145° or 150°–154°. It exhibits muta-rotation, *α*-xylose having $[\alpha]_D$ +79°, falling to +19°, which is the rotation of the equilibrated mixture. The heat of combustion is 561 cals. Bromine oxidises it to xylonic acid, a syrup which is at first lævo-rotatory, but reaches $[\alpha]_D$ +17·5°, as it is transformed into the lactone in solution. It forms a very characteristic insoluble compound $C_5H_9O_6CdBr,H_2O$ with cadmium bromide. Nitric acid in the cold forms an optically inactive trihydroxyglutaric acid.

On reduction, inactive xylitol, a syrup, is formed.

α-Methylxyloside has m.p. 90°–92°, $[\alpha]_D$ +152°; the *β*-isomeride has m.p. 156°–157°, $[\alpha]_D$ −65·9°. With hydrogen cyanide two xylose carboxylic acids are formed, which yield *l*-gulose and *l*-idose on reduction.

The phenylhydrazone has m.p. 116°; the *β*-naphthylhydrazone, m.p. 70°; and the phenylosazone, m.p. 166°.

The methyl pentoses are pentose carbohydrates, in which one of the hydrogen atoms in the primary alcohol group is replaced by methyl. They appear to be widely distributed, but their biochemical significance is not yet understood. They show the same reactions as the pentoses, and, like these, are not fermented by yeasts. Characteristic is the formation of methylfurfuraldehyde on distillation with acids.

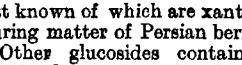
Rhamnose (*Isodulcitol*) $C_6H_{12}O_5,H_2O$, on account of its empirical formula, and the ease with which it crystallised, was formerly classed

with dulcitol and mannitol, hence the original name of *iso*dulcitol. Its chemical behaviour shows it to be a methyl pentose. It appears to be widely distributed in nature in the form of glucosides, the best known of which are xanthorhamnin, the colouring matter of Persian berries and quercitrin. Other glucosides containing rhamnose are baptisin, fisetin, frangulin, fustin, datiscin, glycyphyllin, hesperidin, naringin, rutin, sophorin (*v.* GLUCOSIDES).

It is prepared by extracting Persian berries with hot alcohol, distilling off the alcohol, and heating the xanthorhamnin on the water-bath for 2 hours, with 6 p.c. sulphuric acid. The precipitated rhamnetin is filtered, the filtrate neutralised with barium carbonate, and, after removal of the barium sulphate, evaporated to a syrup. This is diluted hot with absolute alcohol, and the solution allowed to stand, when it deposits hard lustrous crystals of rhamnose. About 15–20 grams are obtained per kilo. of berries.

It is advantageously prepared from the residues of the manufacture of quercitron extract, when these are available.

Rhamnose has the constitutional formula:



the positions of the groups attached to one carbon atom being still uncertain.

The hydrate softens at 89°; m.p. 92°–93°. When anhydrous, it crystallises from acetone in needles; m.p. 122°–126° (Fischer), 108° (Tanret). Like dextrose, it exists in α- and β- modifications, which are in equilibrium in solution. The α-form has $[\alpha]_D$ −17°; the β- form $[\alpha]_D$ +31·5°; and the equilibrated mixture has $[\alpha]_D$ +9°.

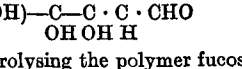
Bromine oxidises it to rhamnonic acid; with nitric acid it yields a mixture of formic, oxalic, and trihydroxyglutaric acids $C_5H_8O_7$. On reduction, the corresponding alcohol rhamnitol is formed.

The phenylhydrazone has m.p. 159°; methylphenylhydrazone, m.p. 124°; ethylphenylhydrazone, m.p. 124°; allylphenylhydrazone, m.p. 135°; amylphenylhydrazone, m.p. 99°; diphenylhydrazone, m.p. 134°; benzylphenylhydrazone, m.p. 121°; β-naphthylhydrazone, m.p. 170°. Rhamnose phenylosazone crystallises in slender yellow needles, slightly soluble in boiling water; m.p. 190°–192°.

Methylrhamnoside has m.p. 108°–109°, $[\alpha]_D$ −62°; acetone rhamnoside, m.p. 90°–91°.

Other derivatives are rhamnose ethylmercaptal, m.p. 135°–137°; rhamnose oxime, m.p. 127°–128°; rhamnose anilide, m.p. 118°.

Fucose $C_6H_{12}O_5$



is obtained by hydrolysing the polymer fucosan, which is a component of the cell-wall of many marine algæ. It is also present in laminaria and Carragheen moss. The seaweed is washed with water and dilute hydrochloric acid, and boiled for 12 hours with 3 p.c. sulphuric acid. The acid is neutralised with baryta, the filtrate concentrated to a syrup, taken up with alcohol, concentrated again, and the sugar isolated as hydrazone.

Fucose crystallises slowly in minute needles, m.p. 130°–140°. It exhibits muta-rotation $[\alpha]_D$ being initially −112°, falling to −74·4° to −77°.

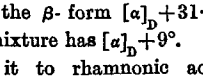
The phenylhydrazone has m.p. 170°–172°; the phenylmethylhydrazone, m.p. 177°; phenylbenzylhydrazone, m.p. 172°–173°; diphenylhydrazone, m.p. 198°; *p*-bromophenylhydrazone, m.p. 181°–184°. Fuconic acid lactone has m.p. 106°–107°, $[\alpha]_D$ +73° to +78·3°.

Rhodeose is the optical antipode of fucose (Müther and Tollens, Ber. 1904, 37, 306). It has $[\alpha]_D$ +73° to +75·2°, and forms derivatives having the same melting-point as those from fucose just described. Rhodeonic acid lactone has m.p. 105·5°, $[\alpha]_D$ −76·3° to −69·4°. Rhodeose is obtained from the glucoside convolvulin.

Chinovose $C_6H_{12}O_5$ is only known as a constituent of the glucoside chinovin, which, on hydrolysis with alcoholic hydrochloric acid, yields ethylchinovoside $C_6H_{11}O_4{\cdot}OC_2H_5$, originally termed chinovite, $[\alpha]_D$ +78°.

Chinovite, when hydrolysed with dilute sulphuric acid, yields chinovose, which is a syrup, showing all the reactions of the carbohydrates. Phenylchinovosazone forms yellow needles; m.p. 193°–194°.

Apiose $C_5H_{10}O_5$ is an altogether remarkable sugar, obtained together with dextrose on hydrolysing the glucoside apiin present in the seeds and leaves of parsley. It contains a branched chain of carbon atoms, having the constitutional formula



(Vongerichten, Annalen, 1901, 318, 121; 1902, 321, 71; Ber. 1906, 39, 235).

It is a pale-yellow syrup, optically inactive, non-fermentable, does not yield furfurol, and yields isovaleric acid when reduced by hydrogen iodide and phosphorus. Bromine oxidises it to apionic acid.

The phenylhydrazone has m.p. 135°; phenylosazone, m.p. 156°; and the bromophenylosazone, m.p. 209°–212°.

Digitoxose $C_6H_{12}O_4$ is obtained on hydrolysing digitoxin, one of the glucosides of digitalis. It crystallises in prisms or plates, m.p. 102°, and is dextro-rotatory. It has the composition (Kiliani) $CH_3{\cdot}CH(OH){\cdot}[CH(OH)]_2{\cdot}CH_2{\cdot}CHO$.

Digitalose $C_7H_{14}O_5$ is similarly obtained from digitalin.

THE CARBOHYDRATE ACIDS

are those containing the same number of carbon atoms as the aldose carbohydrates from which they are derived. They are either mono- or dibasic. Ketoses yield acids with fewer carbon atoms than the original carbohydrate on oxidation.

The monobasic acids are formed on oxidising the aldehyde group to acid, generally by means of bromine or dilute nitric acid. More energetic oxidation converts also the primary alcohol ($-CH_2{\cdot}OH$) group into acid (CO_2H).

Glucuronic acid, which is of importance physiologically, is a type of monobasic acid, in which the aldehyde group is intact, and the primary alcohol group oxidised to acid. The monobasic acids are transformed in aqueous solution, particularly on evaporation on the water-bath, into lactones which crystallise well.

The dibasic acids similarly sometimes form double lactones.

The most important property of gluconic and isomeric acids is their behaviour on heating with pyridine or quinoline, when they are transformed into isomerides, rearrangements of the groups attached to the α-carbon atom taking place. Thus, when gluconic acid is heated with quinoline or pyridine at 130°–150°, it is partially converted into mannonic acid. This behaviour has been of the utmost importance in effecting the synthesis of the carbohydrates.

Gluconic acid $C_6H_{12}O_7$ always contains a proportion of lactone. It is slightly lævo-rotatory at the instant of solution, but becomes dextro-rotatory as the transformation to lactone takes place, the final figure for a mixture in equilibrium of acid and lactone being about +19°. The lactone crystallises in slender needles, m.p. 130°–135°. It has $[\alpha]$ +68° when first dissolved, falling to +19° for the solution in equilibrium with the acid. The calcium salt is sparingly soluble and characteristic, likewise the phenylhydrazide $C_6H_{12}O_6 \cdot N_2H_2Ph$, which forms colourless prisms, m.p. 200°.

Mannonic acid. The lactone crystallises in needles, m.p. 149°–153°, $[\alpha]_D$ +53·8°. The phenylhydrazide has m.p. 214°–216°.

Galactonic acid is obtained by oxidising galactose or hydrolysed lactose with bromine. In the latter case, 100 grams lactose are boiled 4 hours with 400 grams 5 p.c. sulphuric acid, the acid precipitated as barium sulphate, and the filtrate evaporated to 300 c.c., cooled to 35°, and 200 grams of bromine added with constant shaking. After standing for a short time, the excess of bromine is removed by a current of air, hydrogen bromide by lead carbonate and silver oxide, and the solution is saturated with cadmium carbonate, and concentrated till the cadmium galactonate crystallises. The mother liquors yield a second crop, about 50 grams in all being obtained. This salt is purified and decomposed with sulphuric acid.

Galactonic acid crystallises in needles, which, on heating to 100°, lose water, forming the lactone. The lactone crystallises with difficulty; it has m.p. 90°–92°, and forms a crystalline hydrate, m.p. 65°. The acid has $[\alpha]_D$ −10·5°, which becomes −57° on heating. The lactone has $[\alpha]_D$ −70°, and the crystalline hydrate $[\alpha]_D$ −58°. The cadmium salt is characteristic; the phenylhydrazide has m.p. 200°–205°. On heating with pyridine at 150°, galactonic acid is partially converted into *d*-talonic acid.

Lactobionic and **maltobionic acids**, obtained by the action of bromine on the corresponding disaccharides, are colourless syrups or amorphus compounds.

Glucuronic acid (glycuronic acid) $C_6H_{10}O_7$ is frequently found in urine, combined with a variety of substances, forming compounds of a glucosidic nature. It was synthesised by Fischer (Ber. 24, 521), by reduction of saccharic acid lactone, and has the formula

$$CO_2H \cdot [CH \cdot OH]_4 \cdot CHO.$$

It is conveniently prepared from euxanthic acid, which is readily hydrolysed by dilute acids to glucuronic acid and euxanthon

$$C_{19}H_{16}O_{10} + H_2O = C_6H_{10}O_7 + C_{13}H_8O_4.$$

Euxanthic acid, known in commerce as Indian yellow or piuri, is a pigment made almost exclusively in Bengal, and is obtained from the urine of cows which have been fed upon mango leaves (*v.* INDIAN YELLOW).

According to Thierfelder (Zeitsch. physiol. Chem. 11, 388), 1 part of euxanthic acid is heated with 200 parts of water in an autoclave at 120°, the euxanthone separated by filtration, and the solution concentrated. Owing to the introduction of aniline dyes, piuri has become very rare and expensive.

Neuberg and Lachmann (Biochem. Zeitsch. 1910, 24, 416) propose to obtain glucuronic acid by feeding menthol to rabbits. Menthol has the advantage that it is not poisonous, the paired glucuronic acid is fairly easily isolated and readily hydrolysed. 2 grams menthol are dissolved in 1 c.c. alcohol and shaken with 20 c.c. lukewarm water; this emulsion is administered to rabbits, and the urine collected, rendered acid, and extracted with ether. Excess of ammonia is added to the ethereal solution, and the ether distilled off. The residue of insoluble ammonium menthylglucuronate is dissolved in water, precipitated by lead acetate, the precipitate decomposed with hydrogen sulphide, and the filtrate evaporated when pure menthylglucuronic acid is obtained. This is decomposed by boiling with dilute sulphuric acid to give glucuronic acid.

Glucuronic acid is a syrup, and is transformed into the crystalline lactone on evaporation. This is very soluble in water; it has m.p. 175°, $[\alpha]_D$ +19°. It reduces Fehling's solution, yields furfurol on distillation with mineral acids, showing positive reactions with orcinol and phloroglucinol, and is not fermentable.

A number of substances when introduced into the animal body are excreted in the urine as lævo-rotatory-paired glucuronic acid derivatives. These are isolated by precipitation with basic lead acetate, of which an excess should be avoided.

Saccharic acid $C_6H_{10}O_8$

$$\begin{array}{c} OH\,H\;OH\;OH \\ CO_2H{-}C{-}C{-}C{-}C{-}CO_2H \\ H\;OH\,H\;\;H \end{array}$$

is obtained on oxidising dextrose and all carbohydrates which contain dextrose, also from sorbitol, gluconic acid and glucuronic acid. It is prepared from starch or dextrose (50 grams) by heating with nitric acid (350 grams) (sp.gr. 1·15) on the water-bath, and evaporating to a syrup whilst stirring continually. A little water is added, and the solution again evaporated. The residue is dissolved in 150 grams of water, neutralised with a concentrated solution of potassium carbonate, 25 c.c. acetic acid (50 p.c.) added, and the solution evaporated to 80 c.c. On standing, the monopotassium salt separates, and is recrystallised from a little hot water. In the mother liquors, Neuberg (Biochem. Zeitsch. 1910, 28, 355) has recently found 10 p.c. of an acid identical or isomeric with glucuronic acid.

Saccharic acid is a syrup, $[\alpha]_D$ +8°, increasing to +22·5°. The lactone $C_6H_8O_7$ has m.p. 130°–131°, $[\alpha]_D$ +37·9°, decreasing to 22·5° for the equilibrium mixture with the acid. Characteristic is the monopotassium salt $C_6H_9O_8K$,

formed on the addition of acetic acid in excess to a solution of the normal saccharate. This crystallises in small orthorhombic needles, sparingly soluble in water (1·12 parts per 100°). The diphenylhydrazide has m.p. 210°.

The continued action of nitric acid forms tartaric and racemic acids, and, finally, oxalic acid. On dry distillation it decomposes with the evolution of carbon dioxide, yielding pyromucic and *iso*pyromucic acids.

Mucic acid $C_6H_{10}O_8$

$$CO_2H—\underset{H}{C}—\underset{OH}{C}—\underset{H}{C}—\underset{OH}{C}—CO_2H$$

is obtained on oxdising galactose, lactose, raffinose, dulcitol, and all carbohydrates which yield galactose when hydrolysed.

100 grams of lactose are heated on the water-bath with 1200 c.c. of nitric acid sp.gr. 1·15 till the volume is reduced to 200 c.c.; this residue is taken up with an equal volume of water and left to crystallise; the yield is about 38 grams.

Mucic acid is a microcrystalline powder, m.p. 213°–214°; it dissolves in 300 parts of water at 14°, or 60 parts at 100°. It is optically inactive, and cannot be resolved into optically active isomerides.

It forms normal and acid salts with metals, and normal salts with alkaloids. The monophenylhydrazide has m.p. 190°–195°; the diphenylhydrazide, prepared by heating with phenylhydrazine acetate on the water-bath, has m.p. 240°.

The Carbohydrate Alhohols

are widely distributed in the vegetable kingdom, where they occur, as a rule, uncombined with other substances. As a class they are readily soluble in water, crystallise well, and have a small rotatory power. On cautious oxidation they give in turn a reducing sugar, monobasic acid, and dibasic acid. They are obtained by reduction of the corresponding aldose or ketose carbohydrates with sodium amalgam, but, as a rule, owing to transformations in the alkaline solution, a mixture of alcohols is produced. They are not fermentable, and do not reduce Fehling's solution. Only those which occur naturally will be described here, though the alcohols corresponding to the synthetical sugars are known.

Erythritol $C_4H_{10}O_4$

$$CH_2(OH)—\underset{H}{C}—\underset{OH}{C}—CH_2(OH)$$

occurs in a number of lichens, particularly the varieties of *Roccella tinctoria*, where it is present in the form of the ether erythrin $C_{20}H_{22}O_{10}$, which is a diorsellinate of erythritol. This is saponified by boiling with baryta or lime

$$C_{20}H_{22}O_{10}+2H_2O=C_4H_{10}O_4+2C_7H_6O_3+2CO_2.$$

Erythrin is heated for about 2 hours at 150° in a closed iron vessel, with a quantity of milk of lime somewhat less than sufficient to decompose it; the exclusion of air prevents the formation of a large quantity of resinous matter. The liquid filtered from calcium carbonate, on evaporation at a gentle heat, deposits orcinol in fine crystals, and the mother liquors, on further evaporation yield a crystalline mass of orcinol and erythritol, from which the former is extracted by ether (v. De Luynes, Compt. rend. 56, 803). Stenhouse (Chem. Soc. Trans. [2] 5, 222) dissolves the erythrin in a slight excess of milk of lime, boils for half an hour in a vessel with a long condensing tube to exclude air, precipitates the lime in the resulting solution with carbon dioxide, or (on a large scale) by exact neutralisation with dilute sulphuric acid, and evaporates the filtered solution to dryness. On digesting the residue for 20–30 minutes with a mixture of benzene, toluene, &c. (b.p. 110°–150°), in a metallic vessel provided with a condenser, an undissolved portion is left free from orcinol, which, on evaporation and filtering from resin, &c., deposits crystals of erythritol. These may be purified by washing with cold alcohol, pressing, and recrystallising once or twice from hot water.

Erythritol crystallises in large, colourless, transparent quadratic prisms, having an adamantine lustre. Sp.gr. 1·542–1·449. It melts at 126° (Liebermann, Ber. 17, 873), and may be cooled far below its melting-point without solidifying.

It is optically inactive even in presence of borax, and has no action on litmus, but the addition of borax renders it acid. Its taste is sweet, but less so than that of orcinol. It is very readily soluble in water, its heat of solution being at 18°, 5·2 cals., and at 9°, 5·12 cals. (Colson, Compt. rend. 104, 113), sparingly in cold alcohol and insoluble in ether. It does not lose water below 100°, and does not precipitate neutral or basic lead acetate, copper salts, or ammonium lead nitrate (Stenhouse).

Erythritol is not altered by ammonia, by bromine, or by chloride of lime. Heated to 260° with solid potassium hydroxide, it yields oxalic and acetic acids with evolution of hydrogen. With fuming hydriodic acid, it gives secondary butyl iodide $C_4H_8{\cdot}HI$. It is attacked by atmospheric oxygen in presence of platinum black, forming trihydroxybutyric and oxalic acids (De Luynes, Compt. rend. 56, 803; Sell, *ibid.* 61, 741).

With dilute nitric acid, oxalic acid, tartaric acid, and a large quantity of hydrocyanic acid are produced; and with chromic acid and potassium permanganate, or with chromic mixture, formic acid, carbon dioxide, and oxalic acid are obtained (Przybytek, Bull. Soc. chim. [2] 35, 108).

E. Fischer and J. Tafel (Ber. 20, 1088), by the oxidation of erythritol with dilute nitric acid, procured a reducing sugar, erythrose, which formed a crystalline phenylosazone $C_{16}H_{18}N_4O_2$, m.p. 166°–167°, sparingly soluble in water, more readily in ether and benzene. The tetranitrate $C_4H_6(NO_3)_4$ forms large shining laminæ, m.p. 61°.

When erythritol is dissolved in concentrated sulphuric acid, and the mixture heated to 60°–70°, the compound $C_8H_{11}O_2(SO_4H)_3$ is produced, which forms salts with metals (Hesse, Annalen, 117, 329).

Erythritol dissolves easily in chlorosulphonic acid, forming erythritol tetrasulphuric acid $C_4H_6(SO_4H)_4$, which crystallises in snow-white masses consisting of small prisms. It is decomposed by hot water with regeneration of erythritol. The metallic salts are sparingly soluble.

By heating erythritol for about 100 hours with 12–15 parts concentrated hydrochloric acid, De Luynes (Ann. Chim. Phys. [4] 2385; J. 1864, 497) obtained **erythritol dichlorohydrin** $C_4H_6(OH)_2Cl_2$. By raising the temperature to 120°–130°, the result is more quickly

attained, or the compound may be produced by heating erythritol to 120°–130° in a current of hydrochloric acid (Przybytek, Ber. 14, 2072). It melts at 124°–125° (m.p. 145°, De Luynes).

Erythritol tetrachloride $C_4H_6Cl_4$, produced by the action of phosphorus pentachloride, melts at 73°, and crystallises in prisms (Henninger, Bull. Soc. chim. 34, 194; Bell, Ber. 12, 1271). Dinitrodichlorhydrin $C_4H_6(Cl_2)(NO_3)_2O_2$, has m.p. 60°.

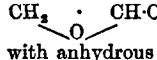
Erythritol dibromhydrin $C_4H_6(Br_2)(OH)_2$ is formed by heating with a saturated solution of hydrobromic acid for 3 hours at 100° in a sealed tube. It is insoluble in water, and melts at 130° (Champion, Compt. rend. 73, 114). Dinitrodibromhydrin $C_4H_6(Br_2)(NO_3)O_2$ is a flaky precipitate, m.p. 75°. It does not detonate under the hammer (Champion).

The tetraformate forms long slender needles, m.p. 150°; the tetracetate has m.p. 85°; and the tetrabenzoate, m.p. 186°–187°.

Characteristic is the dibenzylideneacetal $C_4H_6O_4(C_7H_6)_2$, obtained on shaking with 2 parts of benzaldehyde and 3 parts of 50 p.c. sulphuric acid (Fischer, Ber. 27, 1524), which forms slender needles sparingly soluble in hot water.

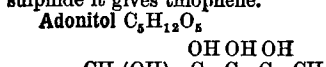
It is not fermentable by yeasts. *Bacterium xylinum* transforms it into a reducing ketotetrose (Bertrand, Compt. rend. 126, 762), and it is attacked by bacteria in cow-dung and hay water, succinic acid in the one case and volatile acids in the other being the main products of change (Fitz, Ber. 11, 1890; 12, 474).

The anhydride $\alpha\delta$-oxy-$\beta\gamma$-butanediol is obtained by heating erythritol for some hours with acids; it is a liquid, b.p. 154°–155° at 18 mm.

The second anhydride $C_4H_6O_2$ was prepared by Pryzbytek (Ber. 17, 1091) by the action of potash on erythritol dichlorhydrin. It is a colourless mobile volatile liquid, b.p. 138°, sp.gr. 1·1322. It combines with water, acids, and ammonia, and forms compounds with hydrocyanic acid and aniline. Its constitutional formula is  .

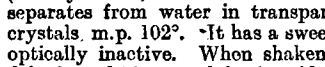
When heated with anhydrous barium oxide for 3 days at 200°–220°, the anhydride yields furfurane; when heated with phosphorus pentasulphide it gives thiophene.

Adonitol $C_5H_{12}O_5$



is the only naturally occurring pentose alcohol; it corresponds to ribose, and is obtained on reducing this. It is found in *Adonis vernalis* (Podwyssotzki, Arch. Pharm. 1889, 141). It separates from water in transparent prismatic crystals, m.p. 102°. It has a sweet taste, and is optically inactive. When shaken with benzaldehyde and 50 p.c. sulphuric acid, the dibenzylidene acetal is formed quantitatively; it crystallises in slender needles, m.p. 164°–165°. The corresponding diformylideneacetal has m.p. 145°. It is oxidised to a mixture of pentoses (Fischer, Ber. 1893, 26, 633; 27, 2491; Merck, Arch. Pharm. 1893, 231, 129).

Mannitol or ***d*-mannite** $C_6H_8(OH)_6$



is the alcohol corresponding to mannose. It was first found in the dried exudation from the manna ash, *Fraxinus ornus*, by Proust, in 1806, and is widely distributed in plants. It is contained in the sap of the larch, in monkshood, in the leaves of *Syringa vulgaris*, in celery, sugar cane, in fungi, where it exceeds dextrose in quantity or even replaces it. Thus *Lactarius pallidus*, when dried, contains from 10 to 15 p.c. (Bourquelot, Compt. rend. 108, 568), and *Agaricus integer* is also a good source. It is prepared from manna by extraction with boiling alcohol. Mannitol is obtained on reducing mannose, lævulose, or dextrose with sodium amalgam.

It crystallises in colourless rhombic prisms, m.p. 166°. 100 parts of water dissolve 16 parts at 16°, 100 parts of alcohol dissolve 0·07 part at 14°. It is optically inactive, but on the addition of borax it becomes strongly dextro-rotatory, a mixture containing 10 p.c. mannitol and 8 p.c. borax having $[\alpha]_D$ +22·5°. This mixture is strongly acid. With caustic soda and other alkalis it becomes lævo-rotatory.

Mannitol has a slightly sweet taste, is not fermentable by yeast, sorbose bacteria oxidise it to lævulose, and it is attacked by many other races. It does not reduce Fehling's solution, or interact with phenylhydrazine.

Mannitol is easily oxidised. Air in presence of platinum black forms mannosaccharic acid, and a mixture of mannose and lævulose, which is also formed with hydrogen peroxide and an iron salt. Bromine gives mainly lævulose. Nitric acid transforms it into mannosaccharic acid and finally into glycollic acid and oxalic acids.

Derivatives.—On heating at 280°, mannitol is converted by loss of water into mannitan $C_6H_{12}O_5$, which is formed at 100° in presence of strong acids. The hexanitrate, also known as nitromannitol $C_6H_8(NO_3)_6$, is prepared by the action of a mixture of sulphuric and nitric acids; it forms colourless acicular crystals, m.p. 112°–113°, $[\alpha]_D$ +40°, which explode violently on being struck or when suddenly heated.

The dichlorohydrin has m.p. 174°, $[\alpha]_D$ −3·75°; and its tetranitrate forms slender needles, m.p. 145°. The hexacetate (Franchimont, Ber. 12, 2059) separates from alcohol in orthorhombic crystals, m.p. 119°–120°, $[\alpha]_D$ +18°. The hexabenzoate has m.p. 149°.

The tribenzylidene acetal crystallises in slender needles, insoluble in water; m.p. 218°–222° (Fischer, Ber. 28, 1975). Triacetone mannitol (Fischer, *ibid.* 28, 1167) forms colourless prisms, m.p. 68°–70°, $[\alpha]_D$ +12·5°. It tastes bitter.

The anhydride mannitan exists in amorphous and crystalline modifications, the latter having m.p. 137°, $[\alpha]_D$ −24°. A second anhydride is mannide $C_6H_{10}O_4$, which exists in several forms. One obtained by reducing the dichlorohydrin crystallises in slender needles or large prisms, m.p. 119°, $[\alpha]_D$ +94°; *iso*-mannide produced by the dry distillation of mannitol *in vacuó*, forms prisms, m.p. 87°, $[\alpha]_D$ +91·4°.

***d*-Sorbitol** or **sorbit** $C_6H_8(OH)_6$

is the alcohol corresponding to dextrose, from which it is obtained on reduction with sodium amalgam in faintly alkaline solution. Sorbitol was discovered in mountain-ash berries by Boussingault (Compt. rend. 1872, 74, 939), and occurs in the fruits of a large number of plants belonging to the *Rosaceæ*.

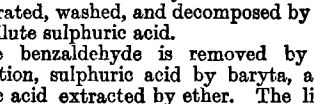
It is prepared from the expressed juice of mountain-ash berries, which is fermented to remove carbohydrate, defecated with basic lead acetate, and concentrated to a syrup *in vacuo*. This syrup is taken up with alcohol, and usually gives crystals of sorbitol. In other cases an equal weight of 50 p.c. sulphuric acid, and a little less benzaldehyde is added, and the mixture agitated. After 24 hours it sets to a crystalline mass of dibenzylidene sorbitol. This is separated, washed, and decomposed by boiling with dilute sulphuric acid.

The benzaldehyde is removed by steam distillation, sulphuric acid by baryta, and the benzoic acid extracted by ether. The liquid is concentrated to a syrup, and inoculated with a crystal of sorbitol (Vincent and Delachanal, Compt. rend. 108, 147). This method permits of the separation of sorbitol in small quantities from plants.

Sorbitol crystallises with 1 mol. H_2O in slender needles, m.p. 55°. The anhydride has m.p. 110°. It is very soluble in water, sparingly so in alcohol. It has $[\alpha]_D - 17{\cdot}3°$; which becomes $+1{\cdot}4°$ in presence of borax. It is faintly sweet, non-fermentable, but is oxidised by *B-xylinum* to sorbose (*q.v.*).

The hexacetate has m.p. 99°. The dibenzylidene acetal as obtained above is a mixture of two isomerides, one of which has m.p. 163°–164°. Triacetone sorbitol has m.p. 45°.

Dulcitol. *Dulcin, Dulcose, Melampyrite, Melampyrin*



is the alcohol corresponding to galactose.

Occurrence.—Found in a manna or crude preparation from a bulbous root of unknown origin from Madagascar (Laurent, Annalen, 76, 358; Jacquelain, *ibid.* 80, 345, in *Scrophularia nodosa* and *Rhinanthus Crista galli* (Eichler, Ueb. d. Melampyrin, Moscow, 1885); in *Melampyrum nemorosum* (Hünefeld, J. pr. Chem. 4, 233; Gilmer, Annalen, 123, 372); in *Euonymus europœa* (Kubel, P. Pharm. Chim. 85, 372), and in dulcite manna (Hecht, Annalen, 165, 148).

Preparation.—Dulcitol is prepared from the Madagascar material by extracting with boiling water and allowing the filtrate to crystallise. To prepare it from the plants above-mentioned, they are gathered at a suitable time and dried. A decoction is made of them, rendered alkaline with milk of lime, boiled, filtered, concentrated, and acidified with hydrochloric acid. Dulcitol crystallises out on cooling. *Dulcite manna* is extracted with boiling alcohol; dulcitol crystallises from the solution filtered hot. The manna yields 72 p.c. dulcitol (Hecht).

Dulcitol may also be prepared by the reduction of galactose with sodium amalgam, the soda produced being from time to time neutralised with sulphuric acid. It is obtained mixed with mannitol on reducing lactose.

Properties.—Dulcitol, both of natural and synthetical origin, crystallises in colourless, highly lustrous monoclinic prisms with octahedral summits. The crystals are gritty between the teeth, and taste very faintly sweet; m.p. 118°. One part dulcitol dissolves in 34·41 parts water at 16·5°; it is but slightly soluble in alcohol, even at a boiling temperature. It is optically inactive, even in presence of borax; the derivatives also are inactive. Its solutions are not coloured brown by potash, nor do they reduce alkaline copper solutions. Nitric acid oxidises it to mucic acid; oxalic and racemic acids are also produced (Carlet, Compt. rend. 51, 137; 53, 343). Yeasts do not ferment it, but other organisms, such as exist in cheese, convert it, in presence of calcium carbonate, into alcohol, lactic, and butryic acids. A saturated solution containing dulcitol and borax in the proportion of 2 mols. dulcitol to 1 mol. borax is neutral, but if the proportion of borax is less, the solution is strongly acid, when the proportion of borax is greater the solution is alkaline (dulcitol being neutral and borax slightly alkaline). A solution of a mixture of dulcitol and sodium paratungstate has an acid reaction after boiling (Klein, Compt. rend. 99, 144).

Dulcitol sublimes partially on careful heating; at 200° it gives off water, and is converted into *dulcitan*; at 275° it decomposes.

Sodium, potassium, calcium, barium, and copper compounds exist.

Neither lead acetate nor subacetate precipitates dulcitol, but a white precipitate is thrown down with an ammoniacal solution of acetate. This is an unstable lead compound.

Dulcitol heated with hydriodic acid in an atmosphere of carbon dioxide yields hexyliodide, water, and iodine.

The hexanitrate is obtained by the action of fuming nitric and sulphuric acids on dulcitol. It crystallises from alcohol in beautiful colourless flexible needles, which melt between 68° and 72°, and give off nitric acid vapours continually, being thereby converted into the tetranitrate. This latter is soluble in alcohol, from which it crystallises in translucent prisms, m.p. 130°–140°, and decomposes at 145°.

Dulcitol forms with hydrochloric acid an unstable hydrochloride $C_6H_{14}O_6{\cdot}HCl,3H_2O$. Similar hydrobromides and hydroiodides exist; they are rather more stable (Bouchardat, Ann. Chim. Phys. [4] 27, 145).

Dulcitol yields chloro- and bromo- hydrins. $C_6H_{12}O_4Cl_2$ crystallises in tables insoluble in water; $C_6H_{12}O_4Br_2$ and $C_6H_{13}O_4BrCl$ are of much the same nature. The corresponding dulcitan bodies $C_6H_{11}O_4Cl$, &c., exist. When these bodies are dissolved in fuming nitric or sulphuric acids, the corresponding tetranitrates are formed, as $C_6H_8Cl_2(NO_3)_4$, &c.

With the acids of the fatty and aromatic groups, dulcitol forms a number of neutral compound ethers. Some of these are ethers of dulcitol and some of dulcitan.

The hexacetate forms hard crystalline plates m.p. 171°; the hexabenzoate has m.p. 147°, both are insoluble in water and ether, sparingly soluble in cold alcohol.

The dibenzylidene acetal forms needles, m.p. 215°–220°. Diacetone dulcitol crystallises in prisms of bitter taste, m.p. 98°.

Perseitol $C_7H_{16}O_7$ was discovered in the fruits of *Laurus persea*, and occurs in *Persea gratissima*. It is identical with *d*-mannoheptitol, synthesised by Fischer (Ber. 23, 930, 2226) by reducing the lactone of *d*-mannoheptonic acid. It crystallises in colourless slender needles, m.p. 188°; dissolves slightly in cold water (6 parts per 100); readily in hot water, and is insoluble in absolute alcohol. It has $[\alpha]_D$ −1·3°, but becomes slightly dextro-rotatory in presence of borax.

Dilute nitric acid in the cold converts it into mannoheptose; the sorbose bacterium oxidises it to a ketoheptose.

The heptanitrate forms needles, m.p. 138°; the heptaacetate has m.p. 119°.

The optical isomeride of perseitol has not been found naturally, but is prepared artificially from *l*-mannoheptose.

Volemitol $C_7H_{16}O_7$ was obtained by Bourquelot by extracting dried *Lactarius volemus* with alcohol. It crystallises in slightly sweet slender needles, m.p. 151°–153°, $[\alpha]_D$ +1·92°, which is not altered on the addition of borax. The constitution is not yet determined.

An **octitol** $C_8H_{18}O_8$ was obtained by Vincent and Meunier (Compt. rend. 127, 760) from the mother liquors of the sorbitol preparation from the fruit of some of the *Rosaceæ*. The syrup had $[\alpha]_j$ −3·42°; the compound with benzaldehyde crystallised in slender needles, m.p. 230°; an isomeride formed at the same time having m.p. 140°.

The Disaccharides.

The disaccharides consist of two monosaccharides, united through an oxygen atom. One residue is fixed through the oxygen of the aldehyde group in just the same manner as is dextrose in the glucosides. In the second residue, the aldehyde or ketonic group may be still present, in which case the junction takes place through one of the alcohol groups, or it may have disappeared, being concerned in the junction. The disaccharides are accordingly of two types. In the first type, in which the aldehyde group is present, they reduce cupric salts, and behave just as dextrose does. In the second type, all these properties are absent. Most of the best-known disaccharides are derived from hexoses.

In establishing the structure of a disaccharide, three points demand attention: (1) the nature of the constituent hexoses; (2) whether it represents an α- or β-glucoside; (3) which hydroxyl- group is concerned in the attachment of the two hexose residues. As a rule, they form no really characteristic derivatives, so that their isolation and identification is far from easy. Those of Type I. contain, like dextrose, an aldehyde group or its equivalent, and since they exhibit muta-rotation and exist in two modifications, there is no doubt that, like dextrose, they possess a closed ring structure rather than a free aldehyde group. In solution, therefore, they exist as an equilibrated mixture of interconvertible isomerides. This is in agreement with their crystallising properties and in marked contrast to the carbohydrates of Type II. *e.g.* sucrose and trehalose, of which only one form exists, and which are characterised by crystallising readily.

Accordingly, both halves of the molecule possess a γ-oxidic structure, but only one section retains the aldehydic grouping potentially functional.

The disaccharides are selectively hydrolysed by enzymes, and are attacked with very different degrees of readiness by mineral acids.

Important conclusions as to their structure are based on this behaviour, for the full discussion of which reference should be made to The Simple Carbohydrates, by E. F. Armstrong, ch. v. and vi. (Longmans, 1910).

The following table gives a list of the di-, tri- and tetra-saccharides and their products of hydrolysis:—

Disaccharides.

Carbohydrate	Components
Type I. *Aldehyde group, potentially functional.*	
Maltose	Dextrose-α-glucoside
*Iso*maltose	Dextrose-β-glucoside
Gentiobiose	Dextrose-β-glucoside
Cellose	Dextrose-β-glucoside
Lactose	Dextrose-β-galactoside
*Iso*lactose	Dextrose-galactoside
Melibiose	Dextrose-galactoside
Turanose	Dextrose and lævulose
Vicianose	Dextrose and arabinose
Type II. *No reducing properties.*	
Sucrose	Dextrose and lævulose
Trehalose	Dextrose (2 mols.)

Trisaccharides.

Type I.	
Mannotriose	Dextrose and galactose (2 mols.)
Rhamninose	Dextrose and rhamnose (2 mols.)
Type II.	
Raffinose	Galactose and dextrose and lævulose
Gentianose	Dextrose (2 mols.) and lævulose
Melezitose	Dextrose (2 mols.) and lævulose

Tetrasaccharides.

Type II.	
Stachyose	Lævulose and dextrose and galactose (2 mols.)

Lactose or milk sugar $C_{12}H_{22}O_{11}$ was first separated from whey by Fabriccio Bartoletti in 1619, and termed *nitrum seri lactis*. It is found in the milk of all mammals. Human milk contains from 5 to 8 p.c. of milk sugar, cow's and ewe's milk, from 4½ to 5 p.c.; mare's and ass's milk, about 6 to 7 p.c. It has not been found in plants.

Lactose is hydrolysed by mineral acids to dextrose and galactose; it is a β-galactoside, that is, the active aldehyde group is in the dextrose residue. It is uncertain whether the primary alcohol group or the α-secondary alcohol group of the dextrose molecule takes part in the union with the galactose residue. Accordingly, lactose has one of the following formulæ:—

$C_6H_{11}O_5$—O·CH_2·CH(OH)·CH[CH·OH]$_2$CH(OH)
(1) O

$C_6H_{11}O_5$—O·CH[CH_2·OH]·CH[CH·OH]$_2$·CH(OH)
O
(2)

The following details of the manufacture of lactose from whey are given by Aufsberg (Chem. Zeit. 1910, 34, 885). Cheese makers usually send their supply of whey to a central factory, where the lactose is separated. Before the whey is concentrated, it is heated and treated with from 1 to 3 p.c. of acid (whey vinegar), in order to coagulate any albuminous substances present. The whey is then concentrated at a temperature of from 60° to 70° under reduced pressure, until it contains about 60 p.c. of total solids; the concentrated liquid is run into rectangular vessels, each holding about 700 litres and surrounded by a cold-water jacket, and after the lapse of 10 hours the thick liquid is stirred, this operation being repeated at intervals. At the end of 24 hours, the pasty mass is submitted to centrifugal action, the crude, moist lactose, amounting to about 3·85 p.c. of the weight of the original whey; a further quantity of crude lactose, amounting to about 0·5 p.c., is obtained by evaporating the mother liquor and allowing it to crystallise. The crude lactose is now refined by dissolving it in water so as to form a solution having a density of 13° to 15°B., adding to the solution a quantity of bone charcoal and about 0·2 p.c. of acetic acid, heating the mixture to 90°, then adding a small quantity of magnesium sulphate, and heating the whole to boiling. The flocculent precipitate is removed by filtration, and the filtrate is evaporated by heating under reduced pressure until it has a density of 35°B. Crystallisation is then allowed to take place, and the crystals are separated. The lactose thus obtained is again subjected to a similar refining treatment, the final yield of crystalline lactose being dried in a centrifugal machine supplied with a current of hot air. The dry product, amounting to about 2·5 p.c. of the weight of the original whey, is then ground and sifted.

Milk sugar is deposited from its aqueous solutions in hemihedral rhombic or monoclinic crystals. The crystals are white, semi-transparent, hard, and grate between the teeth; their sp.gr. is 1·53–1·54. They contain 1 molecule of water ($C_{12}H_{22}O_{11},H_2O$), which they retain at 100° over H_2SO_4, but give up completely at 130°, leaving a colourless melted mass of anhydrous milk sugar, which solidifies in the crystalline state on cooling, and is strongly hygroscopic.

If a solution of milk sugar is evaporated to dryness on the water-bath, an anhydrous milk sugar remains behind, which is not hygroscopic.

Hydrated milk sugar is slightly hygroscopic, soluble in 5 or 6 parts of cold or 2½ of boiling water; from the latter solution the crystals only separate out slowly on cooling. An aqueous solution saturated at 10° has a density of 1·055, and contains 14·55 p.c. of hydrated milk sugar; when left to evaporate it begins to deposit crystals as soon as the density = 1·063, and the solution contains 21·64 p.c. of sugar. It is insoluble in alcohol or ether.

According to Hudson (J. Amer. Chem. Soc. 1908, 30, 1767), lactose hydrate crystallises from aqueous solution at the ordinary temperature, whilst above 95° the β-anhydrous form separates. Schmoeger, and later Hudson, have described three forms of lactose. The α-hydrate $[\alpha]_D+86°$ and the β-anhydride $[\alpha]+35·4°$ both change in solution into the equilibrium mixture or γ-isomeride of constant rotatory power $[\alpha]_D+55·3°$.

Lactose was the first carbohydrate of which more than one modification was observed, and the relationship of these isomerides has been the subject of much discussion (*see* v. Lippmann, Chemie der Zuckerarten). It is to be explained in the same way as the muta-rotation of dextrose.

Lactose loses the water of crystallisation at 130° when heated, turns brown at 160°, begins to decompose at 175°, forming lactocaramel $C_{12}H_{20}O_{10}$, and melts at 203°.

On oxidation with bromine water, lactobionic acid, $C_{12}H_{22}O_{12}$ is formed, and this is converted into galactose and gluconic acid, when hydrolysed by boiling with mineral acids, proving that lactose is a galactoside. Nitric acid first causes hydrolysis, and then forms mucic acid from the galactose, and saccharic acid from the dextrose. Like dextrose, lactose gives rise to two series of derivatives, corresponding to the α- and β-forms of the sugar already mentioned. It contains 8 hydroxyl- groups, and therefore forms octacetates on heating with acetic anhydride and a dehydrating agent. These are colourless, crystalline substances, and well characterised. Other lower acetates are less definitely characterised.

Lactose octacetate may be converted into acetochlorolactose, and this into methyl lactoside, which crystallises in needles, m.p. 171°. The octacetate, obtained by heating with acetic anhydride, crystallises in rectangular plates or needles, m.p. 86° (Herzfeld), 98° (Kremann, Schmoeger), 106° (Fischer and Armstrong), according to the method of purification. It is obviously a mixture. Acetochlorolactose forms prisms, m.p. 57°–59° (Fischer and Armstrong, Ber. 35, 841), $[\alpha]_D^{20}+76·2°$. The isomeride forms prisms, m.p. 118°–120°, $[\alpha]_D^{20}+73·5°$ (*see also* Bodart, Monatsh. 23, 1; Dittmar, *ibid.* 23, 865).

On heating with phenylhydrazine, acetic acid and sodium chloride in a boiling water-bath for 1½ hours, phenyllactosazone $C_{24}H_{32}O_9N_4$ is formed. This does not separate until the solution is cold, and is thus readily distinguished from phenylglucosazone. The yellow needles melt at 200°, and dissolve in 80 parts of boiling water. With very dilute sulphuric acid they form an anhydride $C_{24}H_{30}O_8N_4$, which melts at 223°–224°, and is almost insoluble in water (Fischer, Ber. 20, 830). The phenylhydrazine residues are eliminated by boiling with benzaldehyde, lactosone being formed:

$$C_6H_{11}O_5\cdot O\cdot CH_2\cdot[CH\cdot OH]_3\cdot CO\cdot CHO.$$

This is obtained as a colourless syrup on concentration of the aqueous solution in a vacuum, and is similar in properties to glucosone.

Lactose forms characteristic hydrazones with some of the substituted phenylhydrazines. The amylphenylhydrazone has m.p. 123°; allylphenylhydrazone, m.p. 132°; benzoylphenylhydrazone, m.p. 128°; β-naphthylhydrazone, m.p. 203°.

Alkalis decompose lactose, giving a variety of products. Strong alkalis produce ultimately lactic acid; on fusion with potassium hydroxide, oxalic acid is formed. The prolonged action of lime results in the formation of saccharins (*q.v.*).

Hydrolysis.—Lactose is hydrolysed with difficulty by cold mineral acids, and resists even boiling with weak organic acids. Towards sulphuric acid it is 1240 times as stable as sucrose, and slightly more stable than maltose. Stronger acids hydrolyse it to dextrose and galactose, the optical rotatory power of the solution changing from +52° to +68°.

Lactose is also hydrolysed by an enzyme lactase (*q.v.*) which is present in Kephir grains, in almonds, and in some yeasts. It is not fermented by yeasts, with the exception of a few torula (*S. fragilis*, &c.; *see* Armstrong, Proc. Roy. Soc. 1905, 76 B, 600) which contain lactase. It is more susceptible to bacterial attack, and readily undergoes lactic and butyric acid fermentations.

The synthesis of lactose has not been effected, but an isomeride named provisionally *iso*-lactose, was obtained by Fischer and Armstrong by the synthetical action of Kephir lactase on a concentrated mixture of equal parts of galactose and dextrose. It was isolated as phenyl*iso*-lactosazone. A galactosidoglucose was prepared by the same workers from acetochlorogalactose, and shown to be probably identical with melibiose.

Maltose $C_{12}H_{22}O_{11}$ was perhaps obtained from starch by De Saussure in 1819: it was prepared by Varry, who failed to recognise it as a distinct substance. Dubrunfaut, in 1847, further examined it and gave the name maltose, but regarded it as a trisaccharide. O'Sullivan showed, in 1872, that it is a disaccharide, and gave a fuller description of its characters.

Maltose is primarily a decomposition product of starch, and its occurrence in nature is mainly under conditions where it has been derived from starch. Thus it is found in the leaves of plants, in germinating seeds, and in malt, &c. Under abnormal conditions, it is found in the urine. It is a constituent of commercial glucose. Its occurrence in the form of a glucoside is doubtful; amygdalin does not contain maltose, and it is improbable that lotusin does.

Starch is converted by the enzyme diastase first into dextrins and then into maltose. Diastase also acts on glycogen, forming maltose amongst other products. It is also obtained when starch is hydrolysed by acids, but it is itself hydrolysed in the process to dextrose.

Preparation.—Maltose is always prepared by the action of diastase, usually malt extract, on starch paste: its purification from the dextrins present, which are soluble in alcohol, is often a matter of difficulty. Baker and Day (Brit. Ass. Report, Dublin, 1908, 671) recommend the use of ungerminated barley diastase, which converts starch into maltose, about 60 p.c., and α-amylodextrin: this can easily be separated by one precipitation with alcohol. Precipitated barley diastase is added to a 3 p.c. starch paste, and hydrolysis conducted at 50° for 5 or 6 hours, and subsequently in the cold. The solution is evaporated to a thin syrup and poured into 95 p.c. cold alcohol, so that the resulting strength is about 80 p.c. The α-amylodextrin is precipitated and removed by filtration. The alcohol is distilled off the maltose syrup, seeded with a few crystals, and a little alcohol added. In a few hours it sets to a solid magma of pure maltose. To purify it further the sugar is triturated with strong alcohol, filtered, dissolved in a little water, and poured into boiling 95 p.c. alcohol, again filtered and crystallised from the filtrate.

When malt diastase is used, the procedure is similar, but the entire removal of admixed dextrins requires repeated purification. Maltose of this degree of purity separates readily from strong aqueous solution.

Properties.—Maltose crystallises from water in plates which contain $C_{12}H_{22}O_{11}H_2O$; from alcohol (sp.gr. 0·810) it crystallises in crusts, and at times in cauliflower-like or warty aggregations which contain $C_{12}H_{22}O_{11}$. The hydrate easily parts with its water at 100° in a current of dry air. The anhydride is but slightly soluble in strong ethyl alcohol; it is more soluble in methyl alcohol. The hydrate dissolves more freely in both solvents. Both bodies are very soluble in water, but less so than dextrose. The solution is optically active, the activity being less when the solution is freshly prepared than after standing.

The specific rotatory power for dry maltose is $[\alpha]_j = 154°–155°$, $[\alpha]_D = 139°–140°$ at 15·5° in solutions containing 10 grams per 100 c.c. and under (O'Sullivan, Chem. Soc. Trans. 35, 771, and 45, 5). Meissel (J. pr. Chem. [2] 25, 114) gives the formula

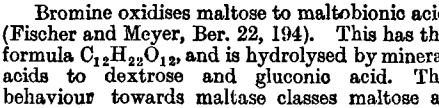
$$[\alpha]_D = 140·375° - 0·01837P - 0·095T$$

to represent the specific rotatory power of dry maltose at 0°, in which P = percentage of maltose in solution, and T the temperature of observation. Brown, Morris, and Millar give +137·93°. The value depends on the concentration as well as on the temperature. The initial rotation is $[\alpha]_D = +119°$. Brown and Morris have shown that maltose is first formed in this low rotatory modification.

Maltose reduces Fehling's solution, 100 parts being equivalent to 62·5 parts of dextrose (O'Sullivan), or 61·9 parts (Brown and Heron, Chem. Soc. Trans. 1879, 35, 618). It is inactive towards cupric acetate (Barfoed's reagent). The density of a solution containing 10 grams maltose in 100 c.c. at 15·5° is 1·0393.

Maltose is hydrolysed on heating with mineral acids to two molecules of dextrose. Sulphuric acid at 80° attacks it 1·27 times as readily as lactose. The weaker organic acids are almost without effect except after prolonged action.

Bromine oxidises maltose to maltobionic acid (Fischer and Meyer, Ber. 22, 194). This has the formula $C_{12}H_{22}O_{12}$, and is hydrolysed by mineral acids to dextrose and gluconic acid. The behaviour towards maltase classes maltose as dextrose-α-glucoside, and the following constitutional formula is provisionally applied:—



The compounds of Maltose.—The octonitrate (Will and Lenze, Ber. 31, 68) crystallises in lustrous needles, m.p. 163°–164°, $[\alpha]_D^{20} = +128°$. The octacetate exists in two isomeric forms. Prepared by heating maltose with acetic anhydride and sodium acetate, it has m.p. 157°

(Herzfeld, Annalen, 220, 200) or 152° (Kremann, Monatsh. 23, 483).

α- and β-heptacetylchloro- and -bromomaltose have been described (Fischer and Armstrong, Ber. 34, 2895; 35, 840; Foerg, Monatsh. 23, 44).

α-Methyl maltoside (Foerg, *ibid.* 23, 44) crystallises in slender plates, m.p. 125°–127°. β-Methyl maltoside (Fischer and Armstrong, Ber. 13, 34, 2895; König and Knorr, *ibid.* 34, 4343) forms concentrically grouped needles, m.p. 93°–95°, $[\alpha]_D^{20}+70°$. β- Phenyl maltoside, m.p. 96°, and menthyl maltoside (Fischer, Ber. 1910, 43, 2521), have also been described.

The hydrazones are not characteristic.

The phenylosazone $C_{24}H_{32}O_9N_4$ is prepared by heating maltose with excess of phenylhydrazine and acetic acid for 1½ hours on the water-bath. It separates after the solution has cooled (difference from dextrosephenylosazone). According to Fischer (Ber. 17, 579; 20, 821) it crystallises in slender bright yellow needles and not in aggregates, having m.p. 206°; Ost (Chem. Zeit. 19, 1503) gives 202°–208°.

J. L. Baker states that the osazone prepared from his pure maltose had m.p. 195°, and consisted entirely of characteristic broad prisms, resembling ribbons in the microscopic field. The stellate aggregates of crystals present in the osazone, from maltose containing traces of dextrin, were absent. Maltosazone does not form an anhydride.

Maltose-*p*-bromophenylosazone has m.p. 198°. The *p*-nitrophenylosazone crystallises in red needles, m.p. 261° (Hyde, Ber. 32, 1815).

Maltose-*p*-diaminobenzoic acid

$$C_6H_3(CO_2H)\begin{matrix}NH\\NH\end{matrix}C_{12}H_{20}O_{10}$$

is formed in small quantities on prolonged boiling of concentrated solutions of the components. It crystallises anhydrous in plates, m.p. 235°, or hydrated with 1 mol. H_2O in needles. The metallic compounds of maltose are amorphous and ill-characterised. It does not form double salts with the alkali chlorides.

Fermentation.—Maltose is fermented only after hydrolysis to dextrose. This hydrolysis is effected by maltase, which is present in most yeasts but absent in *S. Ludwigii*, *S. Marxianus*, *S. exiguus*, *S. membranæfaciens*, some forms of *S. anomalus*, *W. saturnus*, and many others. Accordingly, these yeasts do not ferment maltose. Maltose is also fermented by most moulds, and readily undergoes lactic and butyric acid fermentation.

Synthesis.—Maltose is perhaps formed together with *iso*maltose by the action of concentrated hydrochloric acid on dextrose. It is also formed by the action of emulsin on concentrated solutions of dextrose (E. F. Armstrong, Proc. Roy. Soc. 1905, 76 B, 592). In each case, however, only amorphous or syrupy products could be obtained.

Isomaltose (Revertose, Gallisin) was obtained by Fischer (Ber. 23, 3024, 3687) by the action of 400 grams of cold concentrated hydrochloric acid on dextrose (100 grams) at 10°–15°. It is a viscid syrup, $[\alpha]_D+70°$, and characterised by being non-fermentable and forming a crystalline phenylosazone, m.p. from 140° to 155° (Fischer), according to the purity.

Scheibler and Mittelmeier (Ber. 23, 3075) claimed that the gallisin of Schmitt and Cobenzl (Ber. 17, 1000, 2456) consists mainly of *iso*maltose.

Gallisin is found in commercial glucose. It may be obtained as a white amorphous deliquescent powder, by treating the unfermentable syrup, after evaporation, with absolute alcohol, and finally with ether alcohol. It has a slightly sweet taste; is insoluble in ether, slightly soluble in absolute ethyl alcohol, more easily soluble in methyl alcohol and acetic acid. It reduces silver nitrate, and Fehling's solution; the cupric reducing power of 10·98 grams=that of 5 grams of glucose. It gives no precipitates with solution of lead acetate, mercuric chloride, ferric chloride, or barium chloride. On boiling with dilute acids it is converted into dextrose.

Subsequently, a large number of products obtained in the hydrolysis of starch or of glycogen have been stated to be identical with *iso*maltose, but, failing any characteristic derivative, definite proof of its presence in such cases is lacking (*v.* Lippmann's Chemie der Zuckerarten). It is possible that gallisin and most of these products represent dextrins of low molecular weights or admixtures of these with maltose.

By the action of maltase on a concentrated solution of dextrose, Croft Hill (Chem. Soc. Trans. 1903, 83, 578) has obtained a disaccharide which he terms Revertose. Possibly this is identical with *iso*maltose.

By a similar process, E. F. Armstrong (Proc. Roy. Soc. 1905, 76, B, 592) has obtained an *iso*maltose which, like that obtained by the action of acids, is hydrolysed by emulsin. *iso*Maltose is not attacked by maltase, and the behaviour towards enzymes suggests that it is dextrose-β-glucoside.

Cellose (*Cellobiose*) is prepared by hydrolysis of the octacetate formed by the action of acetic anhydride on filter paper.

To prepare the octacetate $C_{12}H_{14}O_{11}(OC_2H_3)_8$, 7·5 grams of finely divided filter paper are shaken with 20 c.c. acetic anhydride, the mixture cooled to 70°, and at this temperature a mixture of 7 c.c. acetic anhydride and 4 c.c. concentrated sulphuric acid is added. The temperature rises to 110°, the product is poured into 500 c.c. water, and the amorphous acetate collected, washed, and repeatedly crystallised from 95 p.c. alcohol or from ethylacetate. It is ultimately obtained in colourless needles, m.p. 228°.

Five grams are moistened with alcohol and hydrolysed with 15 p.c. alcoholic potassium hydroxide. A granular powder separates: this is dissolved in a little water, excess of alkali neutralised with acetic acid, and the solution evaporated to a syrup, which, after treatment with absolute alcohol and inoculation with a crystal, ultimately yields cellose as a colourless microcrystalline powder. It tastes faintly sweet, dissolves in 8 parts of cold and 1·5 parts of hot water, and reduces Fehling's solution. It has $[\alpha]_D^{20}$ about +25° when freshly dissolved, increasing to +33·7°. It is not fermentable; acids hydrolyse it to 2 molecules of dextrose, as also does the emulsin of almonds.

The phenylosazone forms long yellow needles, m.p. 189°, soluble in 135 parts of boiling water.

Gentiobiose is obtained by the action of invertase or of very dilute acids on the trisaccharide gentianose. It may be prepared from old gentian roots in which this hydrolysis has already taken place by extraction with water and removal of the lævulose by fermentation with top-fermentation yeast. It separates from alcohol in anhydrous crystals, m.p. 190°–195°. It exhibits muta-rotation, the initial value for $[\alpha]_D^{20}$ being +9·6°. It is not fermented by yeast. Emulsin derived, either from almonds or *Aspergillus niger*, hydrolyses it to dextrose. The phenylosazone has m.p. 142°.

Melibiose was first obtained, together with lævulose, by the partial hydrolysis of raffinose (Scheibler and Mittelmeier, Ber. 22, 1678, 23, 1438): this may be effected by dilute acids or certain bottom-fermentation yeasts. Bau gives the following methods of preparation.

20 grams of raffinose in 250 c.c. water are sterilised and fermented for 1 day at 30° with a pure culture of a top-fermentation yeast. The filtrate is sterilised and fermented during several days with a further portion of the yeast. It is then concentrated, poured into hot alcohol, and, after cooling, precipitated with ether. This syrup, after further treatment with alcohol and inoculation, crystallises with difficulty after long standing in the cold.

Alternatively, 20 p.c. solutions of raffinose are hydrolysed by boiling with 2 p.c. acetic acid, and concentrated to a syrup in a porcelain vessel. This is rubbed with 2 vols. of 95 p.c. alcohol, the alcohol decanted, and ether added till a cloud appears. After 2 days, this solution is decanted from any precipitate, inoculated with a few crystals, and set aside in closed vessels.

Melibiose hydrate $C_{12}H_{22}O_{11},2H_2O$ forms doubly refractive monoclinic plates:

$$[a:b:c=1:1·9227:2·0124,\ \beta=77·16°]$$

m.p. 84°–85°. The hydrate has $[\alpha]_D^{20}$ +129·5° as stable value, and shows muta-rotation, the initial value, 5 minutes after solution, being +108°. The anhydride has $[\alpha]_D^{20}$ +143°. It is very soluble in water, sparingly so in ethyl alcohol. Strong acids hydrolyse it to dextrose and galactose: it is slightly more resistant than lactose. It is very sensible to traces of alkali. It is reduced by sodium amalgam to melibiositol, a syrup which is hydrolysed to galactose and mannitol. It is attacked by bottom- and not by top-fermentation yeasts, and thus affords a means of distinguishing between these two varieties of yeast. The former variety contains the enzyme melibiase. It is slowly hydrolysed by emulsin.

The following derivatives are known: phenylhydrazone, light-yellow needles, m.p. 145°; allylphenylhydrazone, m.p. 197°; β-naphthylhydrazone, m.p. 135°; phenylosazone, yellow needles from toluene, m.p. 178°–179°. This dissolves in 110 parts of boiling water, and interacts with benzaldehyde to form melibiosone. The p-bromophenylosazone has m.p. 181°–182°.

Melibiose was the first natural disaccharide to be obtained synthetically (Fischer and Armstrong, Ber. 35, 3144). It was prepared by the interaction of acetochlorogalactose with dextrose.

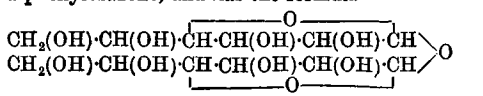
Trehalose (*mycose, trehalabiose*) was originally discovered in ergot, and has since been proved to be very widely distributed in fungi (Bourquelot). It apparently replaces sucrose in those plants which contain no chlorophyll and do not manufacture starch. Trehalose was found in 142 out of 212 species investigated, but only in certain parts of the fungus and at certain stages of the vegetative period. The quantity is a maximum just before the formation of spores. When fungi are picked, trehalose is rapidly converted into mannitol, and after a few hours it has entirely disappeared. The trehala manna from Syria and Persia is stated to contain 20 p.c. of trehalose. To prepare trehalose, suitable fungi (particularly Agaricus and Boletus species) are boiled with much strong alcohol immediately after picking.

Trehalose $C_{12}H_{22}O_{11},2H_2O$ crystallises in lustrous glass-like rhombic prisms

$$[a:b:c=0·6814:1:0·4171;\ \beta=111°\ 31']$$

m.p. 97°. It becomes anhydrous at 130°. It has $[\alpha]_D^{20}$ +178° for the hydrate and +197° for the anhydride, without any muta-rotation. Acids hydrolyse it to 2 molecules of dextrose, but according to Winterstein, only with considerable difficulty, and it contrasts markedly in this respect with sucrose.

It does not reduce Fehling's solution or form a phenylosazone, and has the formula



It is not hydrolysed by invertase and most enzymes, but is affected by a special enzyme, named trehalase, present in most fungi, moulds, and some yeasts, and conveniently prepared from *Aspergillus niger*. Accordingly, trehalose is fermented by those yeasts which contain trehalase. It forms few derivatives: the octanitrate has m.p. 124°, $[\alpha]_D^{18}$ +173·8°; the octacetate has m.p. 97°; the tetrabenzoate, m.p. 81°–83°.

Turanose $C_{12}H_{22}O_{11}$ is obtained from the trisaccharide melezitose, together with dextrose on hydrolysis with 20 p.c. acetic acid solution. The dextrose is destroyed by yeast, and the turanose isolated from an alcoholic extract of the residue in transparent non-crystalline rounded grains of the composition

$$C_{12}H_{22}O_{11}·\tfrac{1}{2}C_2H_6O.$$

They melt at 60°–65°, lose their alcohol at 100° and yield the pure sugar $[\alpha]_D$ +7·18° without muta-rotation (Tanret, Compt. rend. 1906, 142, 1424).

Turanose has a reducing power of 60 (dextrose=100), and is hydrolysed by mineral acids to an equal molecular mixture of dextrose and lævulose, and not to dextrose only, as originally stated by Alekhin (Ann. Chim. Phys. [6] 18, 532). Invertase, maltase, emulsin, and diastase are without action. The phenylosazone has m.p. 215°–220° (Fischer, Ber. 27, 2486). It thus differs from sucrose in containing a free aldehydic group.

OTHER LESS-KNOWN DISACCHARIDES.

Glucoapiose $C_{11}H_{20}O_{10}$ is contained in the glucoside apiin. It has not yet been isolated, as hydrolysis of apiin by dilute acids yields only apiose and gluco-apigenin, and enzymes are without action.

Galacto-arabinose was obtained by Ruff and Ollendorf (Ber. 32, 352; 33, 1806) by oxidation of lactobionic acid from lactose. It is a dextrorotatory syrup: the phenylosazone has m.p. 238°.

Strophantobiose $C_{12}H_{22}O_{10}$ is obtained in the form of the methyl- derivative from the glucoside strophantin (Feist, Ber. 31, 535; 33, 2063, 2069, 2091). It forms colourless crystals, m.p. 207°; does not reduce Fehling, and is not fermentable. Acids hydrolyse it to mannose, rhamnose, and methyl alcohol.

Vicianose $C_{11}H_{20}O_{10}$ is prepared by Bertrand and Weisweiller (Compt. rend. 1910, 150, 180) by hydrolysing the glucoside in the seeds of *Vicia angustifolia* by the enzyme occurring in them. It crystallises in aggregates of small needles, m.p. about 210°; has $[\alpha]_D^{20}+39{\cdot}7°$, the initial value being much higher. It reduces Fehling, and is converted into dextrose and arabinose on hydrolysis.

Diglucose from amygdalin. When amygdalin is hydrolysed by the digestive juice of *Helix pomatia*, the first product is a biose obtained as an amorphous powder. This is non-fermentable, and does not reduce Fehling's solution: it probably has a constitution resembling that of trehalose (Giaja, Compt. rend. 1910, 150, 793–796).

TRISACCHARIDES.

Mannotriose $C_{18}H_{32}O_{16}$ is obtained by the action of either invertase or acetic acid on mannotetrose (stachyose). It is a colourless, faintly sweet crystalline substance, m.p. 150° $[\alpha]_D+167°$. It reduces Fehling's solution. Bromine oxidises it to mannotrionic acid, which is hydrolysed on warming with acids to 2 mols. *d*-galactose and 1 mol. gluconic acid. It is slowly hydrolysed by emulsin and by some yeasts, and is then fermented, but whether completely so is not known.

The phenylosazone has m.p. 192°–194°, according to Neuberg, and not 122° as given by Tanret.

Rhamninose $C_{18}H_{34}O_{14}$ is only obtained from the glucoside xanthorhamnin present in the Persian berry (*Rhamnus infectoria*). In addition to the glucoside, the fruits contain an enzyme, termed rhamninase, which hydrolyses it to the trisaccharide and rhamnetin. Rhamninose forms colourless crystals of faintly sweet taste, m.p. 135°–140°, $[\alpha]_D-41°$; it reduces Fehling's solution. Acids hydrolyse it to galactose and 2 molecules of rhamnose. Sodium amalgam reduces it to the alcohol rhamninitol $[\alpha]_D-57°$, which is hydrolysed by acids to dulcitol and 2 molecules of rhamnose. Bromine oxides it to rhamninonic acid $C_{18}H_{32}O_{15}$, which is obtained, mixed with its lactone, as an amorphous substance; m.p. 125°, $[\alpha]_D-94{\cdot}3°$. It is hydrolysed to *d*-galactonic acid and rhamnose.

This behaviour points to the two rhamnose residues being united in the trisaccharide, but this disaccharide has not been isolated. Rhamninose is not fermentable, and enzymes are without action. The octacetate has m.p. 95°, $[\alpha]_D-31°$.

Gentianose $C_{18}H_{32}O_{16}$ is found in the roots of a number of gentians, from which it is prepared by extracting the fresh roots with 95 p.c. alcohol. It crystallises in colourless plates, m.p. 209°–210°, tastes faintly sweet, and has $[\alpha]_D+31{\cdot}2°$ to $+33{\cdot}4°$.

It does not reduce Fehling's solution, but is hydrolysed by acids to lævulose and 2 molecules of dextrose, the final product having $[\alpha]_D-20{\cdot}2°$. The enzyme invertase hydrolyses it to lævulose and the disaccharide gentiobiose, that of *Aspergillus niger* converts it into dextrose and sucrose.

Raffinose (also termed *melitose*, *gossypose*, *melitriose*) $C_{18}H_{32}O_{16}$ was first discovered by Johnston in 1843, in the manna from *Eucalyptus mannifera*, found in Tasmania. It is often found in considerable amount in the sugar beet, where it was discovered by Loiseau; Ritthausen found it in cotton-seed cake; it is also present in wheat and in oats. To prepare raffinose from molasses, strontium oxide is added until a molecule is present for every molecule of sucrose. After some hours, the strontium saccharate formed is separated by filtration and the liquid heated with excess of strontia, whereby the raffinose distrontionate is precipitated. The strontia compound is decomposed by carbon dioxide, the solution concentrated, and the process repeated to remove most of the sucrose. The syrup finally obtained is dissolved in hot alcohol; the product which separates on cooling is kept under alcohol in a closed vessel, when raffinose slowly crystallises. Raffinose forms small needles, soluble in 6 parts of water at 16°: it is less soluble in ethyl alcohol than sucrose. It is difficult to recognise when it crystallises with sucrose. The hydrate melts at 80°, the anhydrous forms at 118°–119°. The optical rotatory power $[\alpha]_D$ is +104° without muta-rotation. It has no reducing action, and behaves exactly as sucrose. Dilute mineral acids hydrolyse it to lævulose and melibose: strong acids yield a molecule each of lævulose, dextrose, and galactose. Invertase converts it into lævulose and melibiose, emulsin hydrolyses it to sucrose and galactose. Accordingly, the formula is established as:

$$\underbrace{C_6H_{11}O_5}_{\text{Lævulose.}}—O—\underbrace{C_6H_{10}O_4}_{\text{Dextrose.}}—O—\underbrace{C_6H_{11}O_5}_{\text{Galactose.}}.$$

Sucrose. Melibiose.

The undeca-acetyl derivative has m.p. 100°, $[\alpha]_D+92°$.

Melezitose (*melicitose*) $C_{18}H_{32}O_{16},2H_2O$ is found in Briançon manna, which is obtained as an exudation from the young twigs of the larch (*Abies larix*; Fr. *Mélèze*). It was investigated by Berthelot (Ann. Chim. Phys. [3] 55, 282) and by Alëkhine (*ibid.* [6] 18, 532). It is found also in *turanibin* or *terenjabine*, an exudation from *Alhagi maurorum*, growing in Afghanistan, Persia, and in the deserts of the East, and used in Northern India as a laxative (Villiers, *ibid.* [5] 12, 43). This substance is a brown, semi-solid mass, of a slightly sweet taste, due mainly to the presence of dextrose. To obtain melezitose

from this product it is treated with four times its weight of lukewarm water, and the liquid passed through a sieve to separate husks, leaves, &c., and after standing to allow of the deposition of earthy matter, it is evaporated to half its bulk. On standing for a few days, the greater part of the melezitose crystallises out. The crystals are redissolved in twice their weight of hot water, the solution heated on the water-bath, diluted with its own volume of alcohol, heated to boiling to separate earthy and coagulable matter, and filtered whilst hot. On cooling, melezitose separates out and may be obtained pure by two or three recrystallisations. It forms large rhombohedral prisms

$$C_{18}H_{32}O_{16},2H_2O,$$

which effloresce in air and become opaque; they lose the whole of their water at 110°. Dehydrated melezitose has m.p. 148°–150°; 100 pts. of water dissolve of anhydrous melezitose 26·8 pts. at 17·5°; 34·4 pts. at 25°; 75·6 pts. at 100°; sparingly soluble in alcohol, insoluble in ether. The rotatory power is $[\alpha]_D+88·5°$. Melezitose yields no crystalline compounds with alkaline chlorides. On boiling with dilute sulphuric acid it yields *turanose* and dextrose, the rotation falling to +63°. It has no action on an alkaline solution of copper, and is unchanged by diastase or yeast. Nitric acid transforms it into oxalic acid without the intermediate formation of mucic acid. It does not interact with phenyl hydrazine. The undeca-acetate $C_{18}H_{21}O_{16}(OC_2H_3)_{11}$ crystallises in shining monoclinic prisms, m.p. 170°, $[\alpha]_D^{20}+110·4°$.

Stachyose (*Mannotetrose, Lupeose*) $C_{24}H_{42}O_{21}$ was discovered by Schulze and Planta in the tubers of *Stachys tubifera*, and thought to be a trisaccharide. Tanret obtained it from ash manna, and termed it mannotetrose. It has also been found in the twigs of white jasmine and in the subterranean parts of *Lamium album*. It constitutes from 60–75 p.c. of the dry matter of the stachys tubers. The tetrahydrate crystallises in lustrous hard doubly refractive colourless plates ($a:b:c=1·0512:1:0·4213$, $\gamma=90°\ 46'$). It tastes quite sweet and dissolves at 13° in 0·75 parts of water. The anhydride has m.p. 167°–170°, $[\alpha]_D+148°$, without muta-rotation; the hydrate has $[\alpha]_D+133°$.

Stachyose is not acted on by Fehling's solution or by alkalis. Acetic acid hydrolyses it to lævulose and mannotriose. Sulphuric acid converts it into 4 monosaccharides, viz.: 1 molecule lævulose, 1 molecule dextrose, 2 molecules galactose. By the action of nitric acid, about 38 p.c. of mucic acid is formed. Invertase hydrolyses it to lævulose and mannotriose, which latter is slowly attacked by the emulsin of almonds or of *Aspergillus niger*.

According to recent work of Schulze, stachyose is probably identical with the carbohydrate lupeose, present in *Lupinus luteus* and *angustifolius*, as lupeose has $[\alpha]_D+148°$, and gives the same products on hydrolysis.

Neuberg (Biochem. Zeitsch. 1910, 24, 173) prepares it by pressing the juice from the tubers, precipitating impurities with mercuric acetate, removal of the metal by hydrogen sulphide, neutralisation with ammonia, and concentration to a syrup, which is precipitated with alcohol. The precipitate is dissolved in water, impurities precipitated with phosphotungstic acid, and the filtrate concentrated. Barium hydroxide and alcohol are added alternatively. After 24 hours, the barium salt is collected, washed with alcohol, and decomposed by carbon dioxide. Reducing sugars are removed by this treatment and the stachyose readily crystallises.

Polysaccharides.

Glycogen $(C_6H_{10}O_5)n$, the reserve carbohydrate of the animal organism in which it appears to take the place of starch, is a regular constituent of all developing cells. It is present in the liver up to 10 p.c. and in muscle.

Preparation.—Liver is finely minced and thrown into boiling water acidified with acetic acid. The coagulated proteins are filtered off, and the remaining proteins precipitated from the filtrate with trichloracetic acid or potassium mercuric iodide (Brücke's reagent). Glycogen is precipitated from the filtrate with alcohol.

Fresh finely minced liver is extracted for 2 hours with boiling 60 p.c. potassium hydroxide. An equal volume of 95 p.c. alcohol is added to the clear filtrate, containing 15 p.c. KOH, and the precipitated glycogen washed with a mixture of 15 p.c. KOH and 2 vols. of 95 p.c. alcohol.

It is purified in either case by solution and reprecipitation with alcohol, and obtained as an amorphous snow-white powder $[\alpha]_D+191°$, soluble in cold water, giving an opalescent solution. It is not fermentable, does not reduce Fehling's solution, and is not acted on by alkali, even by concentrated solutions at the boiling-point. With iodine it gives a brown-red colouration. Acids hydrolyse it ultimately to dextrose, but dextrins and maltose are formed as intermediate products. Diastase derived from either plants or animals also converts it into dextrins and maltose (*see* Tebb, Journ. of Physiol. 1898, 22, 423).

To estimate glycogen, the tissue is minced and boiled 2–3 hours with 30 p.c. potassium hydroxide. The solution is diluted, filtered, and precipitated with alcohol. The glycogen is again dissolved in dilute alkali and precipitated with alcohol. Finally it is dissolved in water and estimated by hydrolysis with acids into dextrose (1 part = 0·927 parts glycogen) or with the polarimeter.

Inulin. Inulin is widely distributed as a reserve material in plants having tubers or tuberous or fleshy roots, particularly in the autumn in dahlia tubers, Jerusalem artichoke, chicory, garlic, onions, and other plants and bulbs.

To prepare it, a mash is made of the ripe tubers, a little calcium carbonate is added, and the mixture extracted with boiling water. The filtrate is frozen and the sediment which separates dissolved in hot water and again frozen. Tanret advises precipitation with barium hydroxide, decomposition of this precipitate with carbon dioxide and subsequent precipitation with 95 p.c. alcohol.

Inulin, precipitated by alcohol, is a compact colourless powder, resembling starch. The molecular composition is uncertain, as the ordinary methods do not yield trustworthy results. Kiliani gives $(C_6H_{10}O_5)_6,H_2O$;

Brown and Morris, $(C_6H_{10}O_5)_{12},2H_2O$; Düll, $(C_6H_{10}O_5)_{18},H_2O$; Tanret, $(C_6H_{10}O_5)_{30},5H_2O$. It melts at 178°, having $[\alpha]_D$ −38° to −40°, sp.gr. about 1·5. In cold water it is sparingly soluble, but very soluble in hot water, and readily forms supersaturated solutions. It is precipitated by alcohol, when the percentage of alcohol in the liquid reaches 65.

The barium *salt* $C_{36}H_{62}O_{31}\cdot 3BaO$ (Tanret, Compt. rend. 116, 514) is insoluble.

Inulin is hydrolysed by boiling the aqueous solution under pressure, by dilute acids, and also by the enzyme inulase, discovered by Reynolds Green, which is usually present in the same plant when in the germinating condition, but inert in the resting stage. In every case, lævulose is the sole product of hydrolysis. Yeasts are without action.

A number of products are described as lævulins and lævulans, which probably represent polymerides of lævulose of lower molecular weight than inulin.

Manna is the dried saccharine exudation from the stem of the flowering ash, *Fraxinus ornus* and *F. rotundifolia*, small trees cultivated for the purpose in Sicily. A vertical series of oblique incisions is made in the bark when the trees are about 10 years old, the juice slowly exudes and either dries on the stem (flake manna) or in wet seasons drops from the trunk, where it is caught upon tiles or cactus leaves, yielding an inferior variety. Flake manna is obtained in commerce in brittle stalactitic pieces, about 4–6 inches long and 1 inch wide. It is yellowish-white in colour, has a slight agreeable odour and a sweet taste. It is used as a gentle laxative for infants and children.

It consists principally of mannitol (70–80 p.c.): other constituents are mannotetrose (12–16 p.c.), mannotriose (6–16 p.c.) which is formed from mannotetrose, and small quantities of hexoses.

The term is not restricted to the ash, and a number of saccharine exudations of varying origin and composition are classed as 'mannas.' Amongst these are the Persian and Turkestan manna, derived from *Alhagi maurorum* or *camelorum*; the tamarisk manna, also of Persian origin, from the *Tamarix gallica*; oak manna, procured from *Quercus valonia* and *Quercus persicus* in Kurdistan; Australian manna, *Eucalyptus viminalis*; Briançon manna, from the larch, *Larix europœa* in Southern France; Astragalus manna, from various species of astragalus in Persia.

Authorities.—E. von Lippmann, Die Chemie der Zuckerarten, 3rd ed. 1904; L. Maquenne, Les Sucres et leurs principaux dérivés, Paris, 1900; E. Frankland Armstrong, The Simple Carbohydrates, London, 1910; E. Fischer, Untersuchungen über Kohlenhydrate, 1884–1908, Berlin, 1909. E. F. A.

CARBOLIC ACID, *Phenol* $C_6H_5\cdot OH$.

Occurrence and Formation.—Carbolic acid occurs in small quantities in castoreum (Wöhler, Annalen, 67, 360), in urine (Städeler, *ibid.* 77, 18), and is a constant product of the putrefaction of albumen (Baumann, Ber. 10, 685). It is formed when organic substances are strongly heated, and is contained in the tars obtained by the dry distillation of bones, wood (Duclos, Annalen, 109, 163), shale (brown coal), and coal (Runge, Pogg. Ann. 31, 69; 32, 308; Laurent, Ann. Chim Phys. [3] 3, 195).

The tar produced in gas manufacture is the chief and almost exclusive source of carbolic acid. Owing to the demand for carbolic acid as a disinfectant and for the manufacture of dyes and explosives, it has become usual, in tar distillation, to collect a special fraction, the 'carbolic oil' containing as much carbolic acid as possible, before collecting the 'creosote oil,' which contains the other phenolic constituents of coal tar. The 'carbolic oil' begins to come over when the specific gravity of the distillate attains that of water. According to Watson Smith (Chem. Soc. Trans. 1886, 21), ordinary Lancashire coal tar yields about 5 p.c. by volume of crude phenols, containing 65 p.c. by volume of carbolic acid crystallisable at ordinary temperatures.

Coke ovens are now constructed so that the tar produced during the coking of coal can be collected; the following data, having reference to the percentage of carbolic acid in such tars, are given by Lunge (Coal Tar and Ammonia, ed. 1909), which has been largely drawn upon in the compilation and revision of this article: he says, 'The tar from Hüssener's modification of the Carvès oven gave 1·37 p.c. of pure carbolic acid; the tar from the Simon-Carvès oven gave 0·05 p.c. of crude carbolic acid; and similar ovens working with another kind of coal and at higher temperature gave 0·305 p.c. of crude acid. The tar collected from blast furnaces, working with coal (raw) and also that obtained from Mond and Duff producers, contains a high percentage of phenolic constituents, but the quantity of carbolic acid present is very small.'

Carbolic acid can be obtained by fusing potassium benzenesulphonate with caustic potash; the yield is proportional to the temperature and quantity of alkali employed, and is at best (96·23 p.c. of that theoretically possible), when 1 mol. prop. of the former is fused with 6 mol. props. of the latter at 252°. Caustic soda cannot be employed instead of potash, since only a poor yield is obtained by its use (Degener, 7. pr. Chem. [2] 17, 394).

Carbolic acid can also be obtained by heating the diazo- compounds of benzene with water.

Preparation.—Carbolic acid is almost exclusively obtained from coal tar, and is worked up either from the special fraction known as 'carbolic oil' or from the oils intermediate in specific gravity (sp.gr.=1·000–1·020) between the light and heavy oils, that is, distilling between 170° and 230°. The acid is present also in the creosote oils, distilling between 240° and 270°.

The preparation of carbolic acid from coal tar is effected by washing the oils obtained on distilling the tar with a solution of caustic soda, sp.gr. 1·075–1·100, when the tar acids are dissolved as sodium compounds and form a heavy solution upon which the now neutral oils float. It is not advisable to use a stronger solution of caustic soda, as in that case a considerable quantity of naphthalene would also be dissolved. If it is desired to extract carbolic acid only, without any of the higher homologues, the oils are often washed fractionally. For example, a quantity of caustic soda solution more than enough to extract all the carbolic acid but insufficient to take up all the cresylic acid, is

employed, and the phenate of soda solution drawn off is used to wash another portion of oil when the cresylate of soda is decomposed and the cresylic acid is replaced by carbolic acid, and a solution consisting almost entirely of carbolate of soda is obtained.

Another method, suggested by Davis, is to employ, for the first wash, only one-third of the quantity of caustic soda required to extract all the tar acids when carbolic acid only is extracted. In many works, however, the whole of the tar acids contained in the light oil, carbolic oil, and creosote oil fractions are extracted, and after separating the tar acids in one of the ways about to be described, the mixture of carbolic and cresylic acids obtained is separated by fractional distillation. The phenate or carbolate of soda, drawn off from the oil is, in many cases, first purified by blowing steam through it. This carries away naphthalene, neutral oils, and pyridine bases, and the blowing with steam is continued until the water condensing from the escaping steam ceases to have a milky appearance. The purified phenate of soda is then treated with an acid to decompose it and set free the tar acids which float on the surface and are either skimmed off or are separated in an apparatus similar to a Florentine receiver.

Formerly the decomposition was almost always effected by sulphuric or hydrochloric acid, in which case the soda was lost as sulphate or chloride, which it did not pay to recover. The more common practice to-day, however, is to use carbon dioxide to effect the decomposition. If this is used under pressure, complete decomposition is said to be effected, but more generally the process is completed by the addition of a small quantity of sulphuric acid; this is the more necessary, as both carbolic acid and carbolate of soda are mutually soluble in each other.

The separated solution of sodium carbonate, which contains about 1 p.c. of carbolic acid, is recausticised with lime and is used over again to wash another quantity of oil. A twofold saving is thus effected, in that the loss of the soda is avoided and also the carbolic acid which remained dissolved in the sodium sulphate or chloride solution, and was run to waste, is now recovered, inasmuch as it goes forward with the regenerated caustic soda and is regained in the next washing operation. The crude carbolic thus obtained contains, besides phenol (carbolic acid), about 14 to 15 p.c. of water and variable quantities of cresylic acid. It occurs in commerce in three qualities, known as 75's, 60's, and 50's crude carbolic acid, and its value is determined by 'Lowe's' test. This is performed as follows: 100 c.c. of the crude tar acid is slowly distilled in an 8-oz. glass retort, and the receiver is changed when 10 c.c. of oil have come over; these 10 c.c. are accompanied by a varying amount of water, and by reading the quantity of water obtained, the percentage of water is ascertained. The distillation is continued until 62½ c.c. have collected in the graduated tube which is used as a receiver; the distillation is then stopped. The 62½ c.c. are then cooled, and a minute crystal of pure phenol is dropped into the tube, and the cooling continued until the contents begin to crystallise. The temperature is noted when the crystallisation appears to spread through the tube, and this is the measure of the quality of the carbolic acid.

The preparation of pure carbolic acid from the crude article is always commenced by a distillation in wrought-iron stills, formerly without a column, but at the present day fractionating columns are almost universally employed. The water comes over first and then the carbolic acid, which is collected apart, so long as it crystallises on cooling. Some uncrystallisable acid comes over next, and the distillation is then stopped and the residue is mostly pitch.

In some cases, a little strong sulphuric acid and potassium dichromate is added to the contents of the still. The condensing worm must be made of zinc, silver, or stoneware. The distillate is allowed to cool and crystallise, and the crystals are drained from the liquid portion, either on a drainer or in a centrifugal machine. The liquid portion is either sold as liquid carbolic acid or is worked up again with the next batch. The drained crystals are treated with a small quantity of concentrated sulphuric acid and potassium dichromate and redistilled, when 'pure' crystallised carbolic acid of commerce is obtained. In some cases the separation of the last traces of cresylic acid is effected by adding a small quantity of water, and the mixture is cooled, when a hydrate of carbolic acid crystallises out; this is separated from the liquid portion, which contains the cresylic acid and the crystals are redistilled. Water comes over first, and then the boiling-point rises and pure carbolic acid distils over. For medicinal purposes, a final distillation in glass retorts is performed.

Properties.—Pure carbolic acid crystallises in long, colourless needles; has a characteristic odour; melts at 42·5° or 43° and boils at 178·5° (Choay, Compt. rend. 118, 1211); Lunge (Coal Tar and Ammonia, 1909 ed. 210), gives m.p. 42·2° and b.p. 184° under 760 mm. pressure. Ordinary 'pure' carbolic acid of commerce, which contains traces of cresols, melts at a somewhat lower temperature and boils at 182° to 184°. The specific gravity of carbolic acid at 18° is 1·065 (Laurent); its expansion for temperature $t°$ at 760 mm. pressure is stated by H. Kopp as follows:—

$$Vt = 1 + 0{\cdot}0006744t + 0{\cdot}000001721t^2 - 0{\cdot}000000000504081t^3.$$

The presence of small quantities of impurities such as water, naphthalene, or pyridine, materially lowers the melting-point. The red colour of ordinary commercial acid seems to be induced by the presence of minute traces of metals, particularly lead (Meyke, Ber. 16, 2513; *cf.* however, Ebell, *ibid.* 17, Referate 69; Hager, *ibid.* 18, Referate 114; Yvon, Pharm. J. Trans. 1881, 1051; Richardson, J. Soc. Chem. Ind. 12, 415; Bach, Mon. Sci. (A), 8, 508; Kraemer and Spilker, Ber. 1890, 648). Carbolic acid is a deliquescent substance, and in damp air forms a hydrate $C_6H_5{\cdot}OH,H_2O$, which melts at 17·2° (Allen, Analyst, 3, 319). At the same time, however, it is not very readily soluble in water, 100 parts of water dissolving 4·83 parts at 11°; 5·36 parts at 35°; 6·19 parts at 45°; 7·33 parts at 58°; 11·83 parts at 77°; and at 84° both liquids mix in all proportions; whilst conversely, 100 parts of phenol dissolve

23·3 parts of water at 9°; 26·75 parts at 32°; 31·99 parts at 53°; and 40·72 parts at 71° (Alexejeff, Ber. 10, 410). According to Hamberg (*ibid.* 4, 751), however, it dissolves in 15 parts of water at 16°–17°. It is soluble in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerol, olive oil, chloroform, carbon disulphide, &c. The aqueous solution becomes coloured violet by ferric chloride and is without action on litmus. According to Kramers, a mixture of benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, is obtained when the vapour of carbolic acid is passed through a red-hot tube (Annalen, 189, 129). Two isomeric mononitrophenols are obtained by the action of dilute nitric acid (sp.gr. 1·34) (Fritzsche, *ibid.* 110, 150); and at a lower temperature, the *para-* and at higher temperatures the *ortho-* derivative appear to be chiefly formed (Goldstein, Ber. 11, 1943). By the further action of nitric acid, dinitrophenol (Kolbe, 4, 147, 67), and trinitrophenol (picric acid) (Schmitt and Glutz, *ibid.* 2, 52), result.

Chlorine (Laurent, Annalen, 23, 60, 43, 209; Faust and Müller, *ibid.* 173, 303; Benedikt, Monatsh. 4, 233; Benedikt and Schmidt, *ibid.* 4, 606) and bromine (Körner, Annalen, 137, 200, 205, 208, 209, 210; Hübner and Brenken, Ber. 6, 171) convert carbolic acid at the ordinary temperatures into mono-, di-, and tri-substitution derivatives, and at higher temperatures or in the presence of halogen carriers, such as antimony pentachloride, &c., into tetra- and penta- derivatives. The nitro-, chloro-, and bromo- derivatives of carbolic acid are fairly strong acids, and the acid character increases with the number of nitro- groups or chlorine or bromine atoms introduced into the molecule. Iodine yields mono- and di- derivatives in the presence of mercury (Hlasiwetz and Weselsky, Ber. 2, 524) or iodic acid (Körner, Annalen, 137, 213). Sulphuric acid converts carbolic acid into two isomeric monosulphonic acids (Kekulé, Zeitsch. f. Chem. [2] 3, 197), of which the *ortho-* acid is the chief product at the ordinary and the *para-* acid at higher temperatures. When heated with ammonium zinc chloride at 280°–300°, carbolic acid yields aniline, together with diphenylamine and phenyl ether (Merz and Weith, Ber. 13, 1299). When fused with caustic potash, salicylic acid, metahydroxy-benzoic acid and two isomeric diphenols are formed (Barth and Schreder, *ibid.* 11, 1332), whilst fusion with caustic soda results in the formation of pyrocatechol (catechin), resorcinol (resorcin), and phloroglucol (phloroglucin) (*ibid.* 12, 417). The behaviour of sodium and potassium phenates (carbolates), when heated in a current of carbon dioxide, has been studied by Kolbe (J. pr. Chem. [2] 10, 89; *cf. also* Schmitt, J. pr. Chem. [2] 31, 410; D. R. P. 29939, June 24, 1884); with sodium phenate, the reaction commences below 100°, is most rapid and complete about 180°, and continues up to the temperature of the decomposition of sodium salicylate with the formation of that compound as sole product, but with potassium phenate, salicylate is formed only at temperatures below 150°, whilst at higher temperatures the isomeric potassium parahydroxy-benzoate constitutes almost the entire product; in these reactions, one half of the phenol is recovered. When carbolic acid is heated with phthalic anhydride and a dehydrating agent, such as zinc chloride or sulphuric acid, it yields phenolphthaleïn (Baeyer, Ber. 9, 1230; Annalen, 202, 68).

If the acid is heated with oxalic acid and sulphuric acid, it is converted into coralline (Zulkowsky, Annalen, 194, 119; 202, 184), from which pure aurine can be extracted by suitable methods (Dale and Schorlemmer, *ibid.* 196, 77), whilst benzaurine results from heating carbolic acid with benzotrichloride (Doebner-Ber. 12, 1462).

Reactions.—(1) In aqueous solution, carbolic acid gives a violet colour with ferric chloride; this, however, is neither developed in very dilute solutions (Sarauw, Ber. 15, 46) nor in the presence of alcohol (Hesse, Annalen, 182, 161); limit of sensitiveness, 1 in 2000 (Polacci, Ber. 7, 360). (2) The aqueous solution, on treatment with ½ vol. of ammonia and then with a few drops of an aqueous solution of bleaching powder (1 part in 20 parts of water), gives either at once or on standing a blue colouration; limit of sensitiveness, 1 in 4000 (Salkowski, Zeitsch. anal. Chem. 11, 310). (3) Bromine water, added to an aqueous solution of carbolic acid, gives either at once or on standing a yellowish-white flocculent precipitate of tribromophenol bromide (Landolt, Ber. 4, 770); limit of sensitiveness, 1 in 43,700 (*ibid.*), 1 in 80,000 (Lunge). (4) A solution of carbolic acid assumes a deep-red colour when boiled with one-third to one-half its bulk of Millon's reagent (a 10–15 p.c. solution of mercurous nitrate containing nitrous acid); limit of sensitiveness, reaction distinct with 1 in 60,000, and still appreciable with 1 in 200,000. Salicylic acid gives a similar reaction (Plugge, Zeitsch. anal. Chem. 11, 173; Almen, J. 1878, 1079).

Quantitative Estimation.—Carbolic acid occurs in commerce in different qualities; as crude acid, as liquid acid, and as crystallised acid of varying degrees of purity. The percentage of phenols in crude carbolic acid can be approximately determined by shaking it with twice its volume of 10 p.c. soda ley added gradually; the separation of the oily and aqueous layers becomes more accurate if a known quantity of petroleum spirit equal in volume to that of the layer of indifferent and resinous substances, is added, and the amount added afterwards deducted. The phenols are estimated in a portion of the aqueous layer by treatment with hydrochloric acid and subsequent addition of salt to ensure a complete separation. Such a correction is, however, hardly called for, since the phenols will dissolve about as much water as the water will dissolve phenols (Beckurts, Arch. Pharm. [3] 24, 572). Beckurts (*ibid.* [3] 24, 580) also states that Koppeschaar's method (*v. infra*) gives satisfactory results for testing liquid carbolic acid when the specimen is free from cresols. Casthelaz (Bull. Soc. Chim. 42, 574) tests measured samples of crude or liquid carbolic acid in tubes with water, with sulphuric acid (1 to 1), and with soda solution (1 part soda ley (sp.gr. 1·38) to 9 parts of water), and finally fractionates a fourth sample.

The exact quantitative estimation of carbolic acid in the pure product is always made by precipitating it with bromine. The composition of the precipitate was believed to be tribromophenol

(Landolt) until it was ascertained by Benedikt that under certain conditions it was partially composed of tribromphenol bromide (*cf.* Weinreb and Bondi, Monatsh. 6, 506). Koppeschaar's method (Zeitsch. anal. Chem. 15, 233), the one usually employed, requires the following solutions: (*a*) solution of sodium thiosulphate, equivalent to a solution of iodine containing 5 p.c. of iodine; (*b*) solution of starch; (*c*) bromine water (titrated with pure carbolic acid), or preferably a solution of bromine in caustic soda prepared by adding an excess of bromine to the soda and subsequently removing the excess either by boiling (Allen, J. Soc. Chem. Ind. 1884, 64) or by evaporating the solution to dryness and again dissolving in water; (*d*) solution of potassium iodide containing 125 *grams* in the litre. The process consists in treating 25 c.c. of the aqueous solution of carbolic acid (4 grams in the litre) with 100 c.c. either of the solution of bromate and bromide with 5 c.c. of concentrated hydrochloric acid to liberate the bromine, or of bromine water in a stoppered bottle, which is then well shaken, allowed to remain for 15 minutes, treated with 10 c.c. of potassium iodide solution, again shaken, and titrated with thiosulphate. The reactions involved are the following:—

I. $C_6H_5\cdot OH+3Br_2=C_6H_2Br_3OH+3HBr$;

II. $C_6H_5\cdot OH+4Br_2=C_6H_2Br_3\cdot OBr+4HBr$;

III. $C_6H_2Br_3\cdot OBr+2KI=C_6H_2Br_3\cdot OK+KBr+I_2$.

(Weireb and Bondi, *l.c.*); so that, as Beckurts points out (*l.c. infra*), the assumption made by Koppeschaar in the preceding method, that 6 atom. props. of bromine enter into combination with 1 mol. prop. of phenol, is in practice correct. Beckurts (Arch. Pharm. [3] 24, 562) gives the following as the best mode of estimating carbolic acid: The solutions employed are (*a*) 1/20 normal potassium bromide (5·939 grams in the litre); (*b*) centinormal potassium bromate (1·666 grams in the litre); (*c*) potassium iodide solution containing 125 grams in the litre; (*d*) decinormal sodium thiosulphate (24·8 grams of $Na_2S_2O_3,5H_2O$ in the litre). For the titration, 25 to 30 c.c. of the phenol solution (1 in 1000) are treated with 50 c.c. each of the potassium bromate and bromide solutions, shaken with 5 c.c. of concentrated sulphuric acid, allowed to remain 15 minutes, treated with 10 c.c. of the potassium iodide solution, and finally titrated with thiosulphate to estimate the amount of iodine liberated. The calculation is simple: from the 50 c.c. each of bromate and bromide solution, 0·2392 gram of bromine is liberated by the sulphuric acid, and this is capable of converting 0·0469 gram of carbolic acid into tribromophenol; 1 c.c. of the decinormal thiosulphate is equivalent to 0·008 gram of bromine, a quantity capable of converting 0·00156 gram carbolic acid into tribromophenol; multiplying now 0·00156 by the number of c.c. of thiosulphate used, and subtracting the product from 0·0469, gives the weight in grams of phenol in the quantity of solution originally taken. This process is accurate whenever solutions of pure carbolic acid, or mixtures from which the pure acid can be separated, are to be tested, but it fails in all cases (*e.g.* crude carbolic acid) when other phenols, particularly cresols, are also present. Methods for the estimation of carbolic acid have also been proposed by Waller (Chem. News, 43, 152), Degener (J. pr. Chem. [2] 17, 390), and Chandelon (J. Soc. Chem. Ind. 1882, 203); but these are inaccurate (Beckurts). Other methods have been proposed by Moerk (Chem. Zentr. 1904, ii. 1764); Messinger and Vortmann (Ber. 1890, 2753); and Schryver (J. Soc. Chem. Ind. 1899, 553). A biological method for the determination of phenol has been proposed by Blyth and Goodban (J. Soc. Chem. Ind. 1907, 632), and an iodometric method by Skirrow (*ibid.* 1908, 58); and Wake and Inglis have investigated the iodine values of the phenols (*ibid.* 1908, 315). A method has been devised by Allen for determining phenols in carbolic soap (Analyst, 1886, 103).

Uses.—Carbolic acid has powerful antiseptic properties and is used on the large scale as a disinfectant. Large quantities of carbolic acid are also employed in the manufacture of salicylic acid; whilst in the colour industry, a considerable demand for the acid exists, inasmuch as it is the source of picric acid and coraline, and it is used in the preparation of some azo-colours. Phenol has, of late years, been very largely used for the preparation of modern high explosives. 'Lyddite' and 'melinite,' consisting very largely of picric acid and picrates, although trinitrotoluene appears now to be replacing picric acid. Phenol forms condensation products with formaldehyde which are bodies of resinous appearance and properties, and which are proposed as substitutes for natural gums and shellac.

Compounds with Metals.—Potassium phenate $C_6H_5\cdot OK$, formed by dissolving potassium in carbolic acid (Hartmann, J. pr. Chem. [2] 16, 36), or by heating carbolic acid with caustic potash (Baumann, Ber. 10, 686), crystallises in slender white needles, readily soluble in water, alcohol, and ether. Sodium phenate can be prepared by similar methods and may be used in the manufacture of salicylic acid and as a disinfectant. Compounds with barium (Laurent) and lead (Calvert, Zeitsch. Chem. 1865, 531) have also been described. W. H. C.

CARBON. Sym. C. At. wt. 12. Carbon boils at 3600° (Violle, Compt. rend. 1892, 115, 1273; 1895, 120, 868). Carbon occurs in nature in the free state, and very abundantly in combination, notably in the form of carbonates and as an essential constituent of organic bodies. In the free state it is a solid, without taste or smell, exhibiting great diversity in the physical characteristics of its three allotropic forms—diamond, graphite, and charcoal.

The diamond, up to the time of Bergman, was supposed to be a kind of rock-crystal, although Newton regarded it as probably an unctuous substance coagulated. It was shown to be combustible by the members of the Academy del Cimento in 1694, and Lavoisier proved that the sole product of its combustion was carbon dioxide. He had previously ascertained that this gas was a compound of oxygen and an element to which he gave the name of *carbone*, contained in coal and wood. Graphite, as its synonyms, blacklead and plumbago (from the Italian *grafio piombino*—the writing lead), imply, was long considered to be a kind of lead, or as related to antimony; Scheele regarded it as a compound of iron and carbon; Kastner proved that it was essentially carbon. It

combines directly with hydrogen at 1100°-1200°, forming hydrocarbons (Bone and Jerdan, Chem. Soc. Proc. 1901, 162; Bone and Coward, *ibid.* Trans. 1908, 1975; 1910, 1219; Proc. 1908, 222; Pring and Hutton, Trans. 1906, 1591; Pring, *ibid.* 1910, 498). At high temperatures, such as the electric furnace, it is dissolved by the alkaline earth carbides and by rhodium, iridium, palladium, and platinum (Kahn, Compt. rend. 1906, 143, 49; 1907, 144, 197; Moissan, *ibid.* 122, 1479). At the temperature of the electric arc, carbon reduces alumina (Moissan, *ibid.* 1894, 119, 935).

Manufacture of Wood Charcoal.—The earliest plan of *coaling wood*, as the manufacture of charcoal was termed and is still called, is carried on as follows: A piece of ground is levelled at some convenient spot in the forest, which is termed the 'hearth' or 'earth.' In the centre of this a thick pole or bundle of brushwood is placed, around which the wood is arranged, some of the pieces being laid horizontally and others set up at an inclination, or the wood may be placed altogether at any steep angle, sloping outwards from the centre to form a flattened cone, which, when complete, is usually called a heap; the object, whichever way the wood is placed, is to obtain a free circulation of air under the heap to communicate with the chimney in the centre, which is formed by then withdrawing the central pole or bundle of brushwood. The large wood should, if convenient, be at the bottom of the heap, and the outside packed as close as possible; the heap is then covered with small brushwood, and afterwards with turf, or the material most impervious to air which can be conveniently obtained. A fire is lighted in the centre chimney, and by leaving openings in the outside covering at the bottom of the heap, the fire soon extends, and can be guided to any part by making temporary openings to admit the air. When the heap is sufficiently fired, all the openings are closed, and lastly the chimney itself. The fire will always extend most rapidly on the side facing or towards the wind, and great care must be taken to watch and check this, by keeping the covering on that side in good order. The charcoal burner must always be careful to spread the fire as evenly as possible through the heap, and after it is coaled to stop it down carefully; he can always accelerate the process in any part of the heap, if well built, by opening the outside to admit air freely, but if he finds this does not act, from any fault in setting the wood, he had better open a hole with a bar at the place required, and light a fire in the hole; this will soon communicate with the main fire in the heap. As soon as the smoke and white flame cease to escape at the vents, the whole heap must be closed from the air as carefully as possible until the charcoal is quite cooled, and is ready to draw. The fire must never burn too fast; the slower the process, if the fire is steady and regular, the better the yield of charcoal. Hard close-grained woods take a longer time to coal than soft open-grained woods, and should be placed in the heap accordingly. These technical instructions, handed down in the forests for ages as secrets from father to son amongst the 'coalliers' in every country in Europe, are the results of long practical experience, and strictly accord with the true principles on which the process is based.

To carbonise wood under a movable covering, the plan of *meiler*, or heaps, is employed in Germany. The wood is arranged either in horizontal layers or in nearly vertical ones

Fig. 1.

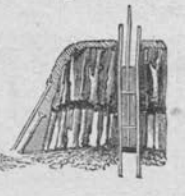


Fig. 2.

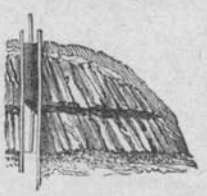


Fig. 3.

with a slight slope, so as to form conical rounded heaps of different sizes. The former are called 'lying *meiler*' (Fig. 1); the latter, 'standing *meiler*' (Figs. 2 and 3). Both are distributed in much the same way.

In districts where the wood can be transported by means of rivers or mountain slides, a dry flat space must be pitched upon (screened from storms and floods), which may be walled round, having a slight declivity made in the ground towards the centre (*v.* Fig. 4). Into this space the tarry acid will partially fall, and may be conducted outwards through a covered gutter beneath into a covered tank. The mouth of the tank must be shut during the coking with an iron or stone slab, luted with clay. A square iron plate is placed over the inner orifice of the gutter to prevent it being choked with coal ashes.

Fig. 4 represents a walled *meiler* station: *a*, the station; *b*, the gutter; *c*, the tank, which is covered with the slab *d*; *e*, a slab which serves to keep the gutter clear of coals. The cover of the heaps is formed of earth, sand, ashes, or such other matter as may be most readily found in the woods. They should be kindled in the centre. From 6 days to 4 weeks may be required for charring a heap, according

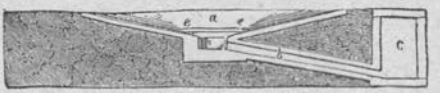
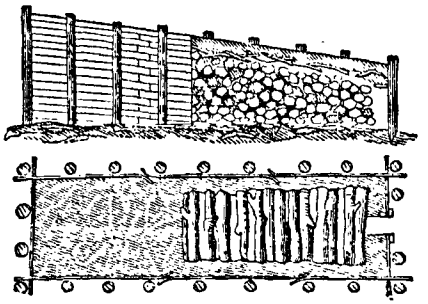


Fig. 4.

to its size, hard wood requiring more time, and the slower the process the better and greater is the product, generally speaking.

Charring of wood in mounds (*haufe* or *liegende werke*) (Figs. 5 and 6) differs from that in the *meiler*, because the wood in the *haufe* is successively charred, and the charcoal is raked out little by little. The product is said to be greater in this way, and also better. Uncleft billets, 6 or 8 feet long, being laid over each other, are covered with ashes, and then carbonised. The station is sometimes horizontal and sometimes made to slope. The length may be 24 feet, the breadth 8 feet, and the wood is laid crosswise. Piles are set perpendicularly to support a roof made of boughs and leaves covered with ashes. Pipes are occasionally laid

within the upper part of the mounds, which serve to catch and carry off some of the liquid.



FIGS. 5 and 6.

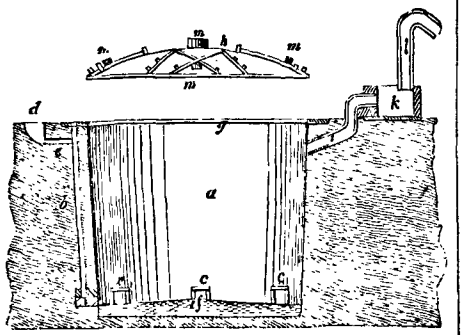


FIG. 7.

Fig. 7 is a vertical section, and Fig. 8 a half bird's-eye view and half cross-section at the height of the pit-bottom, of Chabeaussière's kiln for making wood charcoal. *a* is the oven; *b*, vertical air-pipes; *c*, *c*, horizontal flues for admitting air to the kilns; *d*, *d*, small pits which communicate by short horizontal pipes, *e*, *e*, with the vertical ones; *f*, the sole of the kiln, a circle of brickwork upon which the cover or hood *h* reposes; *i*, a pipe which leads to the cistern *k*; *l*, the pipe destined for carrying off the gaseous matter; *m*, *m*, holes in the iron cover or lid.

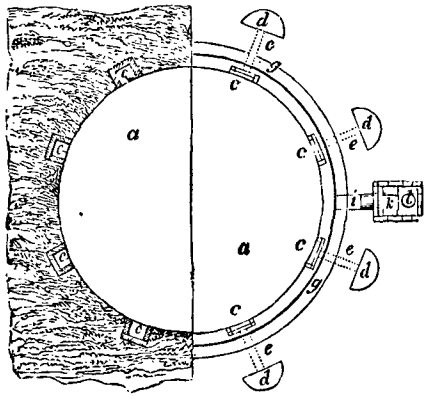


FIG. 8.

The distribution of the wood is like that in the horizontal *meiler* or heaps; it is kindled in the central vertical canal with burning fuel, and the lid is covered with a few inches of earth. At the beginning of the operation all the draught flues are left open, but they are progressively closed as occasion requires. In 8 kilns of this kind 500 decasters of oak wood are carbonised, from which 15,000 hectolitres of charcoal are obtained, equal to 64,000 lbs. French, being about 25 p.c., besides tar and 3000 velts of wood vinegar of from 2° to 3°Baumé.

At Crouy-upon-the-Ourcq, near Meaux, there is a well-constructed kiln for making turf-charcoal. It resembles most nearly a tar kiln. In Fig. 9, *a* is the cylindrical coking place whose surrounding walls are heated by the flame which passes through the intermediate space *b*. The place itself is divided by partitions of fire tiles into three stages, through the apertures in which the flames of the fire, *c*, *c*, rise, and heat the exterior of the coking apartment. In order to confine the heat, there is in the enclosing walls of the outer kiln a cylindrical hollow space, *d*,

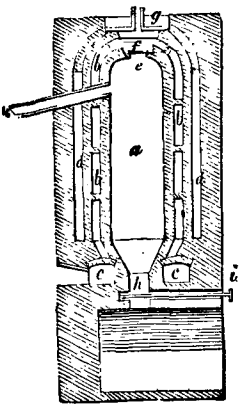
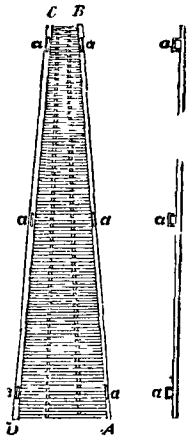


FIG. 9.


C B
a
a
a

wood charcoal is that invented by M. Foucauld, which he calls a shroud or *abri*. To construct one of these, 30 feet in diameter at the base, 10 feet at its summit, and from 8 to 9 feet high, he forms, with wood 2 inches square, a frame 12 feet long, 3 feet broad at one end, and 1 foot at the other end.

The Figs. 10 and 11 will explain the construction. The uprights, A, B, and C, D, of this frame are furnished with three pairs of wooden handles, *a*, *a*, *a*, by means of which they can be joined together, by passing through two contiguous handles a wooden fork, the frame being previously provided with props, as shown in Fig. 11, and covered with loam mixed with grass. A flat cover of 10 feet diameter, made of planks well joined, and secured by four cross-

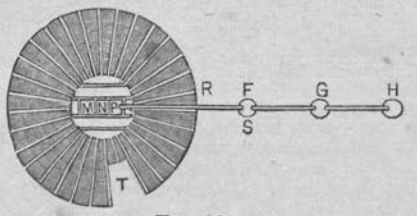


FIG. 12.

bars, is mounted with two trap doors, M, N (Fig. 12), for giving egress to the smoke at the commencement of the operation; a triangular hole, P, cut out in the cover, receives the end of the conduit, Q, R, S (Figs. 13 and 12), of wood

FIG. 13.

formed of three deals destined to convey the gases and condensed liquids into the casks F, G, H. Lastly, a door, T, which may be opened and shut at pleasure, permits the operator to inspect the state of the fire. The charcoal calcined by this *abri* has been found of superior quality.

When it is wished to change the place where the *abri* is erected, and to transport it to a store of new-felled timber, the frame is taken down, after beating off the clay which covers it; the joints are then cut by a saw, as well as the ends of the fork which fixed the frames to one another. This process is economical in use and simple and cheap in construction, since all the pieces of the apparatus are easily moved about, and may be readily mounted in the forests. For obtaining a compact charcoal for the use of artisans, this mixed process of Foucauld is said to be preferable to either the close iron cylinder or the pile.

The fierce process for the production of charcoal, in which the wood is heated in brick kilns shaped like a bee-hive, of 32 feet diameter and 16 feet high in the centre, by means of the combustion of the permanent gases produced during a previous process, is said to produce a far higher percentage of charcoal, and to involve a smaller loss of by-products (Dudley, J. Anal. and Appl. Chem. May, 1891; Armour, Bowers, J. Soc. Chem. Ind. 1892, 152).

The charcoal made at Ontario from the local wood is of excellent quality for blast-furnace use. The wood is here heated in half-iron cylinder retorts, set horizontally and about 9 feet long and 4 feet high. The retorts are charged once a day, and are heated underneath by the tar produced mixed with the waste from the charcoal. The distillate is condensed by straight condensers, one of which is attached to each retort (Goodwin, J. Soc. Chem. Ind. 1902, 743).

In other processes wood is carbonised by superheated steam (Elfetröm, Proc. Inst. Civil Eng. 1906, 164, 60; Zwilliger, J. Soc. Chem. Ind. 1891, 129).

According to Rubands (J. Soc. Chem. Ind. 1902, 1466), a hygienic and antiseptic wood charcoal is obtained by heating a mixture of aromatic plants, such as juniper, thyme, broom, &c., in an oven until the cresols begin to come off. The mass is then thrown into sheet-iron boxes, sealed to prevent combustion, and allowed to cool, the empyreumatic matters thus being reabsorbed.

A large number of improvements in the apparatus employed for obtaining wood charcoal have been proposed (Jones, Eng. Pat. 1485, 1894; J. Soc. Chem. Ind. 1895, 24; Wise Waworth, Eng. Pat. 10522, 1897; *ibid.* 1899, 128; Schenk, Eng. Pat. 23085; *ibid.* 1900, 321; Burcy, *ibid.* 1902, 909; Mourlot, *ibid.* 1902, 1448; Blacher, Chem. Ind. 23, 508).

Charcoal is also prepared from sawdust, wood, chips, and peat. The raw material is fed and pressed into and through heated retorts in a continuous stream, and comes out at the other end of the furnace as hard charcoal. The retorts are provided with pipes for drawing off the by-products (Heidenstam, J. Soc. Chem. Ind. 1898, 445). Many other methods of converting peat into charcoal have been described (Rose, *ibid.* 1896, 643; Eng. Pat. 17568, 1895; Calmont, *ibid.* 1892, 257; Eng. Pat. 3978; Zohrab, *ibid.* 1893, 437; 1897, 1006; Eng. Pat. 3619, 1892; Jürgensen and Bauschlicker, Chem. Zeit. 1901, 25, 635; Stauber, J. Soc. Chem. Ind. 1906, 685; Jürgensen, *ibid.* 1907, 685).

For blast-furnace work, peat charcoal and that obtained from birchwood is the best.

According to Maubér (*ibid.* 1890, 881), charcoal is also produced from the by-products in the manufacture of spirits from grains and cereals. Charcoal suitable for use as filters, respirators, and as wick for candles, can be prepared by placing vegetable fibres, such as cotton, cotton fabric or waste threads into drums, which are placed one by one into an inclined furnace, down which they roll to the lower end, which is provided with an exit door. When no more gases are given off, the drums are withdrawn and the charcoal washed with water (Cooper, J. Soc. Chem. Ind. 1902, 421).

For making gunpowder charcoal the lighter woods, such as the willow, dogwood, and alder, answer best; and in their carbonisation care should be taken to let the vapours freely escape, especially towards the end of the operation, for when they are reabsorbed, they greatly impair the combustibility of the charcoal (Taylor and Challon, *ibid.* 1890, 106).

The charcoal of some woods contains silica, and is therefore used for polishing metals. Being a bad conductor of heat, charcoal is

employed sometimes in powder to encase small furnaces and steam-pipes. It is not affected by water, and hence the extremities of stakes driven into moist ground are not liable to decomposition. In like manner casks when charred inside preserve water much better than common casks, because they furnish no soluble matter for fermentation or for food to animalcules.

For making crayons of charcoal the willow is the best wood that can be employed, as the softness is uniform in all its parts. The durability of charcoal may be seen in several of our old churchyards, where the letters made with lampblack are still perfect, though the white lead with which the body of the stones was painted is entirely destroyed. This property of carbon is shown, however, in a more striking manner by the writings that were found in the ruins of Herculaneum, which have retained their original blackness for two thousand years. The ancients wrote with ink made from ground charcoal.

If it be required to purify any carbonaceous matter to render it fitter for delicate pigments, this may be done by first calcining it in a close vessel, and then lixiviating it in water slightly acidulated by nitric acid.

The incorruptibility of charcoal was well known to the ancients, and they availed themselves of this property upon all important occasions.

Some years ago a quantity of oak stakes were found in the bed of the Thames, in the very spot where Tacitus says that the Britons fixed a vast number of such stakes to prevent the passage of Julius Cæsar and his army. These stakes were charred to a considerable depth, had retained their form completely, and were firm at the heart.

Desmond found that wood charcoal, when submitted to a high temperature out of contact with air, evolved a considerable quantity of gas consisting of 9·14 p.c. CO_2, 18·08 p.c. CO, 49·11 p.c. H_2, 16·04 p.c. CH_4, 0·26 p.c. O_2, and 7·37 p.c. N_2, its antiseptic properties being superior to carbon monoxide (Compt. rend. 1894, 119, 733).

Most of the houses in Venice stand upon piles of wood, which have all been previously charred for their preservation. In this country estates were formerly marked out by charred stakes driven to a considerable depth into the ground. These are occasionally found, and usually the charred portions are quite perfect, although every other part is decayed (*v.* WOOD, DESTRUCTIVE DISTILLATION OF).

Wood charcoal possesses in a remarkable degree the power of absorbing gases in its pores, and in many cases of determining their combination. This power increases with its porosity. As ordinary charcoal contains atmospheric air in its pores, it must for this purpose be prepared by heating it to redness in a close vessel, and cooling over mercury. The following table shows the absorptive power of freshly ignited boxwood charcoal for different gases :—

Ammonia gas	90 vols.
Hydrochloric acid gas	85 „
Sulphur dioxide	65 „
Hydrosulphuric acid	55 „
Nitrous oxide	40 „
Carbon dioxide	35 „
Ethylene	35 „
Carbon monoxide	9·42 vols.
Oxygen	9·25 „
Nitrogen	6·5 „
Hydrogen	1·25 „

Charcoal obtained from the shell of the cocoa-nut has still greater absorptive properties, absorbing, according to Hunter,

Ammonia	171·7 vols.
Carbon dioxide	67·7 „
Carbon monoxide	21·2 „
Oxygen	17·9 „

In consequence of this absorption of gases in the pores of charcoal, their chemical activity is greatly increased. When a piece of charcoal which has absorbed a considerable quantity of sulphuretted hydrogen is introduced into oxygen, a violent reaction immediately takes place, water and sulphur dioxide being set free. If air be employed instead of oxygen, sulphur is deposited.

This property is utilised in the removal of fœtid and bad-smelling gases from rooms, and in the sweetening of bad-smelling liquids and of clothes. For this purpose charcoal of average porosity is found to be the most efficient, and it should be in moderate-sized pieces, its absorbent power being greater in this state than when in fine powder or in very large pieces.

Potassium and sodium alloy absorbs charcoal, and the suspension so obtained has a variety of uses, and constitutes an intermediate product in a variety of processes such as the production of potassium cyanide and so forth (Weintraub, J. Soc. Chem. Ind. 1909, 794).

When charcoal is boiled in a solution of platinum tetrachloride, it becomes impregnated with platinum, and is known as platinised charcoal. This substance possesses in a greatly increased degree the power of inducing chemical combination.

Charcoal containing 2 p.c. of platinum causes oxygen and hydrogen to unite completely in about a quarter of an hour, the rapidity increasing with the percentage of platinum, charcoal containing a larger quantity of platinum acting like platinum sponge. Platinised charcoal may be applied to the preparation of air-filters and respirators, and also as a mild caustic (Stenhouse, Chem. Soc. Trans. 8, 105).

A further property of charcoal is its power of depriving most coloured liquids of their colouring matters, by absorbing them within its pores. The colouring of red wine, cochineal, madder, or indigo, can thus be removed from solutions.

This property was discovered in 1790 by Lowitz, and is made use of on the large scale in several industrial operations, particularly in the process of refining sugar. It is most strikingly possessed by bone-black or *animal charcoal* (*q.v.*). Charcoal of great decolourising power can be obtained by the dry distillation of birchwood or other substances containing carbon mixed with calcium or mangesium chloride, without access of air. The charcoal so obtained is washed with water, then with hydrochloric acid, and then again with water (Ostrejho, J. Soc. Chem. Ind. 1900, 1099; 1902, 58).

Charcoal of higher decolourising power is obtained from blood, horns, hoofs, clippings of hides, glue, &c., in contact with pearl-ash. A good decolourising charcoal is also obtained by

carbonising vegetable matters mixed with chalk, calcined flints, or other earthy substances.

According to Halse (J. Soc. Chem. Ind. 1903, 504), charcoal, especially applicable for use in decolourising and purifying saccharine and other liquids, and which can be used in acid solutions, is obtained by heating wood or a similar material with sulphuric acid to a temperature not exceeding 200°. The charred mass is then washed and dried, and, when spent, it can be revivified by treatment with a smaller amount of sulphuric acid.

Charcoal also precipitates or absorbs certain substances from solution, notably iodine, lime, and its salts (being used for the purification of highly calcareous waters), lead salts and most metallic subsalts, besides many organic substances, as the bitter principles of hop, gentian, and aloe, tannin, alkaloids and resins, from their alcoholic solution (de Coninck, Compt. rend. 130, 1627; Laval, Pharm. J. 1900, 65, 213; Malmegac, J. Pharm. Chim. 1900, 12, 5; Davis, Chem. Soc. Trans. 1907, 1666).

Crude alcohol is occasionally allowed to remain for some time in contact with charcoal.

Carbon is used for the reduction of metals from their ores, and in the manufacture of glass for the reduction of alkaline sulphates.

Porous carbon can also be used with advantage in electrolytic cells (Löb, Zeit. f. Elect. Chem. 1896, 3, 185). When used as an anode in strong hot sulphuric and other acids, which give off oxygen at the anode, carbon is dissolved, and this property can be used for depositing carbon on suitable cathodes (Coehn, J. Soc. Chem. Ind. 1897, 445).

(For the treatment of carbon articles before use, compare Thomson Houston, *ibid.* 1905, 1230; Eng. Pat. 28062, 1904; Acheson, U.S. Pat. 749418, 1904.)

Gas-carbon (*Glance coal*) is a very dense form of carbon, deposited in the upper part of the retorts in the manufacture of coal gas and in blast furnaces. It often exhibits the lustre and sonority of a metal, is very hard, and a good conductor of heat and electricity. It is used to form the negative element in a bunsen battery.

Materials used for manufacture of carbon electrodes are coke, hard and soft pitch, coal tar, and petroleum oil; in some cases, to obtain electrodes of better mechanical wearing power, a small portion of the coke is replaced by soot. The proportions of the various substances depend on the kind of electrode required. Roush (J. Ind. Eng. Chem. 1909, 1, 286; Lake, J. Soc. Chem. Ind. 1900, 1001; Cooper, Shrewsbury and Marshall, *ibid.* 1896, 25; Starks, *ibid.* 1906, 544; U.S. Pat. 819606, 1906).

According to Nieworth (J. Soc. Chem. Ind. 1894, 1206), carbons of less resistance and greater illuminating power when used in arc lamps, can be obtained by mixing the carbon with aluminous earths, magnesia, or other metalliferous minerals before moulding, after which process it is heated by means of an electric current. The carbon, when being heated, is supported in a holding sleeve of non-conducting material to prevent warping. Castner (J. Soc. Chem. Ind. 1894, 1067; Acheson, *ibid.* 1894, 407) adds 10 p.c. carbide of silicon to the carbon used for arc lamps. Rivers (*ibid.* 1906, 483; Kuffrath, *ibid.* 1907, 309) adds yttrium salts. Langville (*ibid.* 1892, 935) describes a process for obtaining carbon for electrical purposes from paper pulp (Eng. Pat. 13847, 1892).

Carbon filaments are also prepared for use in incandescent lamps and electric lamps (Thomson Houston, J. Soc. Chem. Ind. 1905, 62; Pring and Fielding, Chem. Soc. Trans. 1909, 1497; Chatelier and Wolagdine, Compt. rend. 1909, 148, 1715; Howell, Electrician, 1905, *55*, 588; Levis, J. Soc. Chem. Ind. 1905, 721, 882; Eng. Pat. 6959, 1904).

Lampblack is prepared on the large scale by burning fat, oil, resin, tar, &c., with an imperfect supply of air, either in a brick furnace or in cast-iron chambers.

The resulting dense black smoke is conducted into large chambers, where, on account of the extremely sluggish draught, it is allowed to roll about until the particles gradually coalesce into masses which after some time fall on the floor as soot. The condensation of the particles may be greatly facilitated by sending a current of electricity through the atmosphere of smoke, or else it can be agitated by mechanical means (Irvine, J. Soc. Chem. Ind. 1890, 1110).

When commercial lampblack is strongly heated, a large amount of empyreumatic matter is given off, which condenses into a brown greasy mass consisting of chrysene, pyrene, capnomar, &c. This causes ordinary lampblack to cohere when pressed. After calcination it loses this property.

Creosote or other suitable carbonaceous fuel is burnt in a furnace with an adjustable air supply, and the products of combustion are sent through a cooler, where by-products are condensed in centrifugal separators, the carbon deposited being collected in underlying receivers (Adam, J. Soc. Chem. Ind. 1907, 701; Eng. Pat. 13301, 1906).

An arrangement of lamps for the preparation of an especially fine quality of lampblack from waste fat and mineral oils is described in Payen-Paul, 64, 65.

Numerous improvements in the apparatus for the production of lampblack have been described (Wegelin, J. Soc. Chem. Ind. 1898, 747; 1899, 925; 1900, 56; 1902, 1022; 1903, 1190; 1908, 81, 579; Fr. Pat. 380983, 1907; Irvine, J. Soc. Chem. Ind. 1890, 1110; Sanders, *ibid.* 1900, 753; Lembdner, *ibid.* 1903, 1238; U.S. Pat. 741726, 1903; Smith, J. Soc. Chem. Ind. 1909, 430; Meiser, *ibid.* 1908, 1212; D. R. P. 203711; Lennard, J. Soc. Chem. Ind. 1899, 1009; Ogilvy, *ibid.* 1902, 1084).

Carbon has also been obtained direct from smoke (Ward, *ibid.* 1897, 902). Irvine (*ibid.* 1894, 532) obtains lampblack by spraying tars or oils rich in carbon over incandescent coke, mixing the gases so produced with air and steam, and burning them with a limited supply of air.

Lampblack, carbon black, also sometimes spoken of as gasblack, hydrocarbon black, jet-black, and so forth, is used in the production of printer's ink, paints, mineral-black, stove polish, shoe leather, rubber goods, fertilisers, colouring cement, mortar pulp, and artificial stone, harness oil, stenciling, &c. It varies in composition and properties with the material and method used in its production. When produced from the natural gas in American oil wells, the

carbon-black differs from ordinary lampblack, by mixing with water on being shaken with it; ordinary lampblack will not do this. It is also quite different in appearance from lampblack obtained from oils, having a fine velvet-like gloss.

(*See* description of figure and apparatus for manufacture, Cabot, J. Soc. Chem. Ind. 1894, 130. *Cf.* also Purtle and Rowlands, *ibid.* 1908, 234; U.S. Pat. 877596, 1908; Prosch, J. Soc. Chem. Ind. 1903, 640.)

A good lampblack, said to be superior to the best American blacks, is also obtained by sparking a mixture of hydrocarbon under pressure and with or without admixture of carbon di- or mon-oxide (Koppers, J. Soc. Chem. Ind. 1906, 13; Machtolf, *ibid.* 894, 1909; 482, 1050; D. R. P. 207520, 1907; Gollwert, J. Soc. Chem. Ind. 1909, 1050). According to Frank (*ibid.* 1900, 545; 1905, 29, 1044), the carbon, at the moment of liberation, is readily taken up by metals; it can thus be made to pass into silver, imparting to the latter the appearance of so-called oxidised silver.

According to Peters, lampblack suitable for use in the preparation of paints, can also be obtained by heating the waste carbons from arc lamps to 1200°–1400°, and then allowing the mass to cool slowly (*see* also *Acetylene black*).

Carbon monoxide; *carbonous* or *carbonic oxide*; *formic anhydride* CO; sp.gr. 0·96716 (Rayleigh), 0·96702 (Leduc) (air = 1). V.D. 14. (−186°) (Wroblewski, Compt. rend. 98, 982). S.H.p. 0·2346. S.H.v. 0·16844 (Wiedemann; Pogg. Ann. 157, 1). C.E. 0·003667 (Regnault). S. (6°) 0·0287; (9°) 0·0269; (18·5°); 0·02315 (Bunsen). S. alcohol (2°) 0·20356; (13°) 0·20416; (16°) 0·20566; (24°) 0·20452 (Bunsen); $\mu_0 = 1{\cdot}000301$; $\mu_2 = 1{\cdot}00035$; $\mu_0 = 1{\cdot}000391$ (Croullebois, Ann. Chim. Phys. [4] 20, 136). Does not exactly obey Boyle's law; $PV/P_1V_1 = 1{\cdot}00293$ (Regnault). Its critical temperature is −139·5°, and the corresponding pressure 35·5 atmospheres. It boils at −190°.

Discovered by Lassonne, and independently by Priestley. Composition first established by Clement and Desormes.

Carbon monoxide is present in coal and water gas, from both of which it is sometimes obtained industrially (Williams, J. Soc. Chem. Ind. 1891, 270; Claus, *ibid.* 1890, 170).

Produced by the oxidation of charcoal at high temperatures. By the reduction of carbon dioxide by means of hydrogen, carbon, metals, &c., at a red heat, or over carbon made incandescent electrically and coated with a bad conducting material (Engels, J. Soc. Chem. Ind. 1901, 350). In the reduction of metallic oxides by charcoal or coke. By the dry distillation of many organic compounds, and together with hydrogen and carbon dioxide when steam is passed over red-hot charcoal. By passing electric sparks through carbon dioxide (Buff and Hofmann, Annalen, 113, 140) or by heating carbon dioxide to 1300° (Deville, Compt. rend. 59, 873). By heating dehydrated oxalic acid, or by heating dry alkaline formates and acetates with formic acid (Lorin, *ibid.* 82, 750). By heating an oxalate or formate or these acids with concentrated sulphuric acid.

Carbon monoxide is also produced in considerable quantities from various explosives, such as mellinite, gun cotton, &c. It is evolved by an alkaline pyrogallol solution during the absorption of oxygen, unless a large excess of potash is employed (Clowes, Chem. Soc. Proc. 1895, 200).

Prepared by the decomposition of oxalic or formic acid, potassium ferrocyanide, or potassium cyanide, by concentrated sulphuric acid (Boudouard, Compt. rend. 1899, 128, 98, 307, 822; Wade and Panting, Chem. Soc. Trans. 1898, 257).

(1) $C_2H_2O_4 = CO + CO_2 + H_2O$.

(2) $CH_2O_2 = CO + H_2O$.

(3) $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4$.

In the first case the gas is mixed with carbon dioxide, which must be removed by passing through potash or lime-water. In the last reaction it is quite free from carbon dioxide, but if the temperature is too high, a quantity of sulphur dioxide is produced in addition to the carbon monoxide. It is liable also to contain a small quantity of hydrocyanic acid vapour.

Dry calcium oxalate or barium oxalate is mixed with about $\frac{1}{10}$ dry lime, and strongly heated, the gas passed through lime and dried: $CaC_2O_4 = CaCO_3 + CO$, any carbon dioxide formed being absorbed by the lime. Carbon monoxide is evolved in the manufacture of carbides, and is collected and stored, It is also produced in the decomposition of sugars.

Carbon monoxide is manufactured practically pure by bringing a mixture of oxygen and carbon dioxide in contact with incandescent graphite, coke, anthracite, &c. As thus obtained, it may be used for the manufacture of special steels, the reduction of refractory oxides, the treatment of iron ores in the blast furnace, and for other purposes (Loiseau, J. Soc. Chem. Ind. 1908, 1112; Fr. Pat. 390673, 1908).

Properties.—Colourless, tasteless gas, combustible, non-supporter of combustion. Absorbed by carbon, by several metals, and by a solution of cuprous chloride in hydrochloric acid or ammonia. It acts as an energetic reducer. It is a highly poisonous gas, producing giddiness, and ultimately asphyxia when inhaled. 0·43 p.c. in air is fatal to man (Mosso, J. Gas Lighting, 1902, 80, 1334); 0·2 p.c. is also poisonous if breathed for any time.

When carbon monoxide is passed over dry silver oxide, the latter is reduced thus: $CO + Ag_2O = Ag_2 + CO_2$. Ammoniacal silver oxide is also reduced, and the reaction may be employed for the detection of small quantities of carbon monoxide in air (Dejust, Compt. rend. 1905, 140, 1250; Berthelot, *ibid.* 1891, 112, 597; Habermann, Zeitsch. angew. Chem. 1892, 324).

0·02 p.c. carbon monoxide may be detected by the decolouration of a mixture of silver nitrate, and weak permanganate solution acidified with nitric acid (Merwet, Compt. rend. 1897, 124, 621).

According to Gréhant (*ibid.* 1891, 113, 289; 114, 309), 1 part of carbon monoxide may be detected in 10,000 parts of air, by aspirating the air through dog's blood, and testing the respiratory capacity of the blood before and after the experiment. When the air is passed under a pressure of 5 atmospheres, the test becomes still more delicate. It can also be detected by passing the gas through palladium chloride, when a

metallic precipitate is formed and the colour indicates the quantity present. $\frac{1}{50000}$ to $\frac{1}{350000}$ carbon monoxide can be detected in the atmosphere by passing several litres of the suspected air through iodic acid, when the following reaction occurs:—

$$5CO+2HIO_3 = 5CO_2+H_2O+I_2.$$

The *iodine* is absorbed in chloroform or carbon disulphide, when the relative tint indicates the quantity of carbon monoxide, or else the carbon dioxide is absorbed by standard potash solution and the carbon monoxide calculated (Gautier, Compt. rend. 1898, 126, 793, 871, 931, 1299; St. Martin, Compt. rend. 14, 1036; Kinnicutt and Sandford, J. Amer. Chem. Soc. 1900, 22, 14; Fillanger, Chem. Zeit. 1903, 27, Rep. 126; Levy and Pécoul, Compt. rend. 1905, 140, 98; Fr. Pat. 349714, 1904; 142162, 1906; Morgan and McWhorter, J. Amer. Chem. Soc. 1906, 29, 1589; Goutal, Ann. Chim. anal. 1910, 15). Clowes recommends the flame cap test as an accurate and rapid method for detecting carbon monoxide (Brit. Assoc. Report, Chem. Zeit. 1896); whilst to detect the presence of carbon monoxide in mines, Haldane and also Herman (J. Soc. Chem. Ind. 1896, 854) recommend the use of mice, which are very rapidly affected by small quantities of carbon monoxide.

According to Leblanc (Ann. Chim. Phys. [3] 5, 223), it is chiefly the presence of this gas that causes the poisonous action of air in which charcoal has been burnt. A small proportion of carbon monoxide in a dusty atmosphere constitutes a dangerously explosive mixture. It combines with the red colouring matter of the blood-forming carboxyhæmoglobin, and may be recognised by its absorption spectrum, which is almost identical with that of oxygenated blood, and is characterised by two bands between D and E. On the addition of ammonium sulphide, these disappear in the case of oxygenated blood, and the spectrum shows one band midway between D and E, but remains unchanged if carbon monoxide is present (Vogel, Ber. 11, 235; Hoppe-Seyler, Zeitsch. anal. Chem. 3, 439; also Preyer, J. 1867, 802; Nawrocki, J. 16, 640; Gréhaut, Compt. rend. 87, 193; St. Martin, *ibid.* 1892, 114, 1006). According to Nicloux (*ibid.* 1898, 126, 1526, 1595), carbon monoxide is a normal constituent of dog's blood, but this has been denied by Buckmaster and Gardner (Proc. Roy. Soc. B, 1909, 81, 515). Carbon monoxide burns ordinarily with a blue flame, which, by previous heating, becomes red, generating carbon dioxide. The temperature of its flame in air is about 1400° (Valerius, J. 1874, 58). When dry it is not changed by the electric current nor by ignited platinum wire, but when standing over water it is decomposed by a glowing platinum spiral (Buff and Hofmann, Chem. Soc. Trans. 1860, 12, 273). When not absolutely dry, it may be exploded with oxygen by the electric spark or by platinum wire heated to 300° or by spongy platinum at ordinary temperatures. 2 vols. CO unite with 1 vol. O, forming 2 vols. CO_2.

Dixon (Phil. Trans. 1884, 617) has shown that no action takes place when a spark is passed into a mixture of perfectly dry carbon monoxide and oxygen, but that a mere trace of moisture renders the mixture explosive. The combination takes place very slowly in presence of small quantities of steam, and increases in rapidity with the quantity of steam present. Probable reactions:

$$2CO+2H_2O = 2CO_2+2H.$$
$$2H_2+O_2 = 2H_2O.$$

Hence the steam acts as a carrier of oxygen to carbon monoxide (*v.* Dixon, Chem. Soc. Trans. 49, 94).

Small quantities of other gases than steam were tried: if the gas contained hydrogen, explosion occurred, if the gas contained no hydrogen, no explosion occurred. When a mixture of carbon monoxide and steam is heated to about 600°, a portion of the carbon monoxide is oxidised. If the carbon dioxide is removed as it is formed, the whole may be oxidised. L. Meyer's experiments (Ber. 19, 1099) seem to prove that a dry mixture of carbon monoxide and oxygen can be exploded if a very strong spark is used, and a sufficiently high temperature then obtained, and if the gases are under considerable pressure. When sparks from an induction coil are passed through a mixture of carbon monoxide and steam, carbon dioxide, a little formic acid, and sometimes carbon, are formed (Dixon, Chem. Soc. Trans. 49, 94). When to a mixture of dry carbon monoxide and hydrogen, oxygen insufficient for complete combustion is added, and the mixture exploded by the spark, carbon dioxide and steam are formed in a ratio dependent upon the shape of the vessel and the pressure up to a certain limit, called the 'critical pressure.' Above this pressure the ratio of the formation of carbon dioxide and water is independent of the shape of the vessel. The critical pressure becomes lower the larger the quantity of oxygen used. The ratio $CO+H_2O : CO_2+H_2$ remains constant so long as the vol. of the hydrogen is more than twice that of the oxygen, provided no steam condenses, and the pressure is above the critical pressure. When the vol. of hydrogen is less than twice the vol. of oxygen, the above ratio diminishes. The presence of an inert gas increases the formation of carbon dioxide and diminishes that of water, hence it lowers the value of the ratio $CO+H_2O : CO_2+H_2$. This ratio is called the 'coefficient of affinity' of the reaction (Dixon, Phil. Trans. 1884, 617; Chem. Soc. Trans. 49, 94). According to Brodie, when carbon monoxide and hydrogen are submitted to the action of the silent discharge, marsh gas is formed by synthesis; when pure and dry carbon monoxide is circulated through the induction tube, it is decomposed, carbon dioxide being formed together with other 'oxy-carbons' of the formulæ C_4O_3 and C_8O_4 (Brodie, Proc. Roy. Soc. 21, 245).

Carbon monoxide is converted into carbon dioxide under the influence of nascent oxygen from chromic acid (Ludwig, Annalen, 142, 47), but not by ozone, either in diffused daylight or in direct sunshine (Remsen and Southwark, Amer. J. Sci. [3] 11, 136). It is likewise oxidised by palladium charged with hydrogen in presence of oxygen and water (Traube, Ber. 15, 2325, 2854; 16, 123; Remsen and Keiser, *ibid.* 17, 83); by mixing with oxygen and passing over platinum black; by nitric oxide (Hasenbach, J. pr. Chem. [2] 4, 1); by heating with metallic oxides and with many oxysalts.

When passed over finely divided metals, such as nickel, cobalt, or iron, the quantity of carbon dioxide formed depends on the temperature and the metal (Zimmermann, Ber. 1903, 36, 1231; Sabatier and Senderens, Bull. Soc. chim. 1903,

29, 294; Berthelot, Compt. rend. 1891, 112, 594; Van Breakedensen and Horst, Rec. trav. chim. 19, 27; Smits and Wolff, Zeitsch. physikal. Chem. 1903, 45, 199; Charpy, Compt. rend. 1903, 137, 120; Boudouard, *ibid.* 1899, 128, 1522). In some cases a volatile carbonyl compound is formed of the type $M(CO)_4$ (Lange and Quincke, Chem. Soc. Proc. 1890, 112; 1891, 117; Wartha, Chem. Zeit. 1891, 15, 915; Garnier, Compt. rend. 1891, 113, 189; Gautz, Bull. Soc. chim. 1892, 13, 278; Bertholet, 1892, 431, 434; Sabatier and Senderens (*l.c.*). According to Gautz (Compt. rend. 1892, 114, 115), at 400° carbon monoxide reacts with manganese and iron, thus: $CO+Mn = MnO+C$. Carbon monoxide passes through cast and wrought iron when heated to redness, and, according to Siverts and Kramftaar (Ber. 1910, 43, 893), it dissolves in nickel and cobalt, but not in copper.

Minute quantities of carbon monoxide reduce gold chloride, and also gold, silver, and mercury oxides (Fay and Secker, J. Amer. Chem. Soc. 1903, 25, 641).

When an electric spark is sent through a mixture of ammonia and carbon monoxide, ammonium cyanate is chiefly formed (Northall Laurie, Chem. Soc. Trans. 1905, 433).

Pure carbon monoxide forms a colourless transparent liquid under 200–300 atmospheres at −139°, and solidifies to a snowy mass *in vacuo* at −211° (Olszewski, Compt. rend. 99, 706; 100, 350; Wroblewski and Olszewski, Ann. Chim. Phys. [6] 1, 112).

Carbon monoxide combines with potassium at about 80° to form an explosive compound, KCO (Brodie, Chem. Soc. Trans. 1860, 12, 269). It is rapidly absorbed by a solution of cuprous chloride in ammonia or hydrochloric acid, by which means it may be directly estimated in a gaseous mixture (*cf.* Thomas, Chem. News, 37, 6). According to Mauchot and Brandt (Annalen, 1909, 370, 286), it forms the compound $CuCl\cdot CO,2H_2O$, with copper chloride, and the $2H_2O$ can be replaced by $2NH_3$. It is also absorbed by moist silver oxide. It unites directly with chlorine, forming phosgene gas (Schützenberger, Zeitsch. f. Chem. [2] 4, 321). It is absorbed by heated potassium hydroxide at about 200°, forming potassium formate (Berthelot, Ann. Chim. Phys. [3] 61, 463). Fröhlich and Geuther (Annalen, 202, 317) recommend passing carbon monoxide over soda-lime for this purpose. It combines with sulphur to form carbon oxysulphide; with platinum tetrachloride to form $C_2O_2PtCl_4$ and $C_2O_2PtCl_2$ (Schützenberger, Ann. Chim. Phys. [4] 21, 430). It is rapidly absorbed by anhydrous hydrocyanic acid cooled by a freezing mixture, two layers being formed, but the gas is evolved on removing the tube from the mixture (Böttinger, Ber. 10, 1122). It acts on metallic alcoholates with formation of acids by synthesis (Geuther, Annalen, 202, 288; Schroeder, *ibid.* 221, 34).

Carbon monoxide has been used in electrolytic cells by Haber and Moser (Zeitsch. Elektrochem. 1905, ii. 593).

Carbon dioxide, *Carbonic anhydride, Carbonic acid. Gaseous.*—Sp.gr. 1·52909 (Rayleigh); 1·52894 (Leduc). V.D.; 22·42 at 800°; 21·2 at 1180° (Meyer and Goldschmidt, Ber. 1882, 15, 1165).

Specific heat (const. vol.), 0·33 (equal vol. air = 1); 0·2169 (equal wt. air=1) (Regnault, Compt. rend. 36, 676, etc.; Wiedemann, Pogg. Ann. 157, 24). Ratio of specific heat at const. press. to specific heat at constant volume =1·29–1·305 (Amagat and Röntgen, Compt. rend. 71, 336; 77, 1325). Coefficient of expansion=0·0037 (Regnault, Magnus, and Joly). $PV/P_1V_1=1·00722$ (Regnault, *ibid.* 20, 975); at 200° carbon dioxide obeys Boyle's Law (Amagat, *ibid.* 68, 1170; 73, 183).

$\mu_0=1·000395$; $\mu_R=1·000356$; $\mu_c=1·000496$ (Croullebois, Ann. Chim. Phys. [4] 20, 136; Chapman and Rivière, Compt. rend. 103, 37). Heat of formation (const. press.) $(C+O_2)$ =96·96; $(CO+O)$=67·96: heat of formation (const. vol.) $(C+O_2)$=96·96; $(CO+O)$=67·67; $(C+O_2+Aq)$=102·84; $(CO+O+Aq)$ = 73·84; $(CO_2 + Aq)$ = 5·88; $(CO_2Aq + n\text{NaOHAq})$ = 11·016 (n=1); 20·184 (n=2); 20·592 (n=4) (Thomsen).

Solubility of CO_2 in water (Bunsen, Annalen, 93, 1):—

at 0°=1·7967	at 7°=1·3339	at 14°=1·0321
1°=1·7207	8°=1·2809	15°=1·0020
2°=1·6481	9°=1·2311	16°=0·9753
3°=1·5787	10°=1·1847	17°=0·9519
4°=1·5126	11°=1·1416	18°=0·9318
5°=1·4497	12°=1·1018	19°=0·9150
6°=1·3901	13°=1·0653	20°=0·9014

whence absorption coefficient

$$=1·7967-0·07761t+0·0016424t^2.$$

Solubility of CO_2 in alcohol:—

at 3·2°=4·0442	at 14·3°=3·3257
6·8°=3·7374	18°=3·0391
10·4°=3·4875	22·6°=2·8277

whence absorption coefficient

$$=4·32955-0·09395t+0·00124t^2$$

Liquid.—Sp.gr. 1·057 at −34°; 0·966 at −11°; 0·84 at +11°; 0·726 at +22·2° (Cailletet and Mathias, Compt. rend. 102, 1202). Coefficient of expansion very large, 120 vols. at −20° become 150 vols. at +30° (Thilorier, Ann. Chim. Phys. 60, ii. 427).

Critical temperature 30·9° (Andrews, Phil. Trans. 1869, 575), 31·35° with a corresponding pressure of 72·9 atmos. (Amagat); 31·9° and a pressure of 77 atmos. (Dewar). Vap. press. in atmos. (Regnault) 17·1 at −25°; 30·9 at −5°; 35·4 at 0°; 40·5 at +5°; 52·2 at 15°; 66 at 25°. B.p. −78·2° at atmos. press. (Regnault).

Solid.—Sp.gr. slightly under 1·2 (Landolt, Ber. 1884, 17, 309). Vap. press. in atmos. (Faraday) 5·33 at −57°; 2·2 at −70·5°; 1·14 at −99·4°. When solid CO_2 is exposed to the air, the temperature remains constant at −78° to −79° (Villard and Jarry; Pouillet; Regnault).

Carbon dioxide was known to Paracelsus and Van Helmont, and was carefully studied by Black. Its true composition was first demonstrated by Lavoisier in 1775. It was liquefied by Davy and solidified by Thilorier. It is formed by the combustion of carbon in oxygen or air (Dixon, Chem. Soc. Proc. 1899, 118; Nauwaan, Zeitsch. angew. Chem. 1896, 200). According to Potter (Proc. Roy. Soc. 1908, 80, B, 239), amorphous carbon, such as charcoal, lampblack, coal, &c., when exposed to air, is

slowly oxidised by the agency of bacteria, to carbon dioxide, the amount of which increases with rise in temperature. The temperature at which carbon will form carbon dioxide and monoxide, when heated in oxygen, depends largely on whether the temperature has been reached by heating or cooling (Manville, Compt. rend. 1906, 142 1190). The presence of moisture is necessary for the combustion of carbon in oxygen (Brereton Baker, Chem. Soc. Trans. 1885, 349). Is a constant product of ordinary processes of combustion. It is also formed by the respiration of animals, in various processes of fermentation, and by the decay of animal and vegetable substances. It is evolved from fissures in the ground in volcanic districts, and from the craters of active volcanoes, and exists in solution in natural waters, some of which contain it in such quantities as to effervesce. It is found also in mines, quarries, wells, and caverns, particularly in limestone districts. It is a constant constituent of the atmosphere, which contains on the average about 0·034 p.c. The air in streets often contains as much as 0·05 to 0·09 p.c. In crowded rooms it may reach 0·3 p.c. It is further produced by the decomposition of carbonates either by the action of heat or of stronger acids, and is frequently formed when organic bodies are subjected to high temperatures. In the reduction of many metallic oxides by carbon; by burning carbon monoxide; by heating together carbon monoxide and steam; and by the action of steam on calcium carbonate at red heat; by heating a mixture of potassium dichromate and sodium carbonate.

Best prepared by acting on chalk, marble, or magnesite with dilute hydrochloric acid solution. The gas may be collected over water or by displacement of air. On the large scale it is obtained by heating chalk or limestone to redness in iron or earthen vessels (in lime burning) or by burning charcoal. It is manufactured also as a by-product in the combustion of fuel. Also pure on large scale by heating carbonates with steam (J. Soc. Chem. Ind. 3, 568).

According to Thom and Pryor (*ibid.* 1909, 1087), pure carbon dioxide can be manufactured from limestone by the following process: The limestone is heated in closed retorts around a central combustion chamber, beneath which is a furnace, the whole apparatus being enclosed in a casting which excludes air from the retorts. Superheated steam is admitted to the retorts at their lower ends, and this decomposes the limestone and carries the carbon dioxide through outlets at the top of each retort, leading to a collecting gas main running round the top of the casting. The retorts have closely fitting mouthpieces, at which they are charged and discharged respectively. By a system of air and waste-gas flues, perfect combustion and the fullest use of heat from the waste gases is ensured (Eng. Pats. 20102, 24332, 1908).

Carbon dioxide is obtained commercially from natural waters from the Saratoga springs in New York, and also in South Germany. In North Germany the gas is obtained by the combustion of coke, which is generally considered to be the cheapest and best commercial method of producing carbon dioxide. Coke is burnt in a generator, A (Fig. 14); the products pass into a combustion chamber, B, into which hot air is admitted to complete the combustion, thus oxidising all the carbon monoxide and hydrogen sulphide. The hot gases now pass through tubes contained in the vessel C, thus heating and decomposing the bicarbonate solution contained in this vessel. The gas now passes through one or more wash towers, D, containing lime-

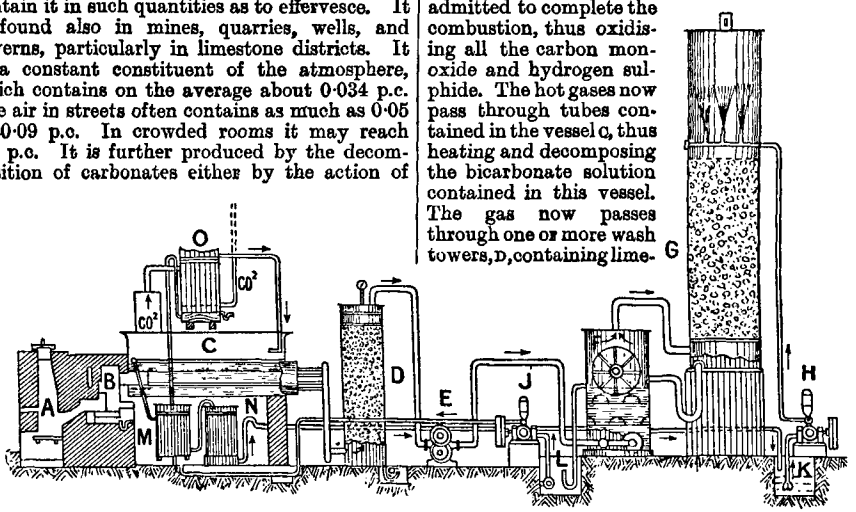


FIG. 14.

stone over which water trickles, and is freed here from dust and sulphur dioxide. E is a blower or fan, which sucks the gas through the furnace and drives it through the absorbing apparatus. F is a rectangular vessel filled with potash ley, and provided with a number of semicircular baffle plates, so arranged that the gas accumulates under each successively, thus remaining exposed for a considerable time under the pressure of the column of fluid to a large surface of liquid. The absorption is further helped by an agitator, which throws the liquid into the upper portion of the vessel. From F the gas passes into the tower G, where the absorption is practically completed, and then leaves the apparatus. The circulation of the potash ley starts from the tank K, whence it is pumped by H through the Körting's jets into the upper part of G, which is thus filled with fine spray. The siphon at the bottom of the tower delivers the partially saturated ley into F, which it leaves, almost saturated, by the overflow siphon and accumulates in the tank L. The pump J then drives it through the tubular vessels M and O (where it is heated to 60° and 90° respectively) into the heater C, where its temperature is raised to 100°. The 'poor ley' circulates in the opposite

direction back to the tank K. The carbon dioxide evolved from C passes into a cooler, then to a gasholder (Schwatolla, Zeitsch. angew. Chem. 1900, 1284).

Other methods of obtaining carbon dioxide from coke are described by Candia and Merlini (J. Soc. Chem. Ind. 1908, 847), Leslie (*ibid.* 1905, 240), Gravillon (*ibid.* 1900, 164; Eng. Pat. 8377, 1904), and many others.

Numerous patents also exist for obtaining carbon dioxide from furnace gases and from lime kilns, most of which depend upon its absorption by potassium or sodium carbonate solution, from which it is then boiled off (Rylands, J. Soc. Chem. Ind. 1892, 1005).

Leslie (*ibid.* 1907, 688) describes a somewhat different method. The furnace gases pass from a purifier to a pump, where they are compressed, after which they are cooled in a heat interchanger, from which they are led to a drying vessel, containing calcium chloride, into a refrigerator, in which the carbon dioxide is condensed to snow; the other gases, still above their critical temperature, are passed back through the interchanger, whilst the carbon dioxide is liquefied and drawn off into tubes and cylinders (Eng. Pat. 11902, 1906).

A method of obtaining sterilised carbon dioxide, with disinfecting properties, is described by Bouchaud-Praceiq (J. Soc. Chem. Ind. 1908, 994).

Many attempts have been made to collect the carbon dioxide given off during fermentation processes, but none of these has been successful so far from a commercial or industrial point of view.

Mixtures of a carbonate or bicarbonate with a salt or double salt, which is readily hydrolysed in aqueous solutions, have been prepared for the generation of carbon dioxide (Menter and Sedlitzky, J. Soc. Chem. Ind. 1908, 1151; Eng. Pat. 14863, 1908).

Ageron and Remy (J. Soc. Chem. Ind. 1906, 847) have prepared a compound by heating a mixture of magnesium sulphate and sodium sulphate or bisulphate with sulphuric acid, which they use as a substitute for acids in liberating carbon dioxide from carbonates.

Carbon dioxide is a colourless, inodorous gas, neither combustible nor a supporter of combustion. Strongly heated potassium or sodium and brightly burning magnesium burn in carbon dioxide.

When quite dry it has no action upon litmus, but if moisture be present the litmus is coloured wine-red. The colour disappears on exposure to air, owing to escape of the gas. Passed into lime-water, carbon dioxide renders it turbid, owing to the formation of calcium carbonate, but if the gas be in excess, the neutral carbonate is converted into an acid carbonate, and the liquid becomes clear.

Carbon dioxide is rapidly absorbed by a solution of caustic potash.

Between −85° and +54° absolutely dry carbon dioxide does not react with absolutely dry alkali hydroxides. At or above 54°, the dry substances do react, and at 85° a trace of moisture at once starts the reaction, which is completed very rapidly (Moissan, Compt. rend. 1903, 136, 723). It is also absorbed by sulphuric acid [$100\alpha=926$], where α=Bunsen's absorption coefficient (Bohr, Chem. Zentr. 1910, ii. 1414).

Its solution in water has a sp.gr. 1·0018. It has a slightly acid taste, colours litmus wine-red, and partially neutralises alkalis and dissolves carbonates of barium, strontium, calcium, and magnesium, &c.

The solution corrodes iron. Kröhake (J. Soc. Chem. Ind. 1900, 520) found that water containing about 40 mgrms. of CO_2 per litre reduced iron pipes in a short time from 26 mm. to 7 mm. diameter, owing to the formation of a brown crust, the pipe itself being corroded to a depth of 1-3·5 mm.

Its solution in water probably contains carbonic acid H_2CO_3. At ordinary temperatures, and under 1 atmosphere, the mass of carbon dioxide dissolved increases as the pressure. But at pressures of 2, 3, or more atmospheres, the mass of carbon dioxide dissolved is less than that calculated by Dalton and Henry's law (*v.* Khanikoff and Louguinine, Ann. Chim. Phys. [4] 11, 412). By the action of carbon dioxide under pressure on water at low temperatures, the crystalline hydrates $CO_2,6H_2O$ (Villard, Compt. rend. 1894, 119, 368), $CO_2,8H_2O$, and $CO_2,9H_2O$ (Hempel and Seidel, Ber. 1898, 31, 2997) have been obtained.

Water which has been saturated with carbon dioxide under pressure gives it up as soon as the pressure is removed. This property is made use of in the manufacture of effervescing drinks and aërated waters (*v.* AËRATED WATERS).

Under the same pressure the volume of gas absorbed by water diminishes as the temperature rises, the whole of the gas being expelled at boiling heat. Hence carbonic acid water, holding an earthy carbonate in solution, deposits it when the water is boiled. This is the cause of the furring of kettles, boilers, &c., in which spring or river waters have been boiled.

Potassium burns in carbon dioxide at a red heat with a red incandescence, depositing charcoal mixed with potassium carbonate. Sodium decomposes it in a similar manner, as do phosphorus and boron in presence of an alkali.

It is decomposed by the electric spark into carbon monoxide and oxygen, if hydrogen, or mercury, or some other metal is present to combine with the oxygen, otherwise the carbon monoxide and oxygen recombine to form carbon dioxide (Collie, Chem. Soc. Trans. 1901, 1063).

Partly decomposed by electric sparks, a condition of equilibrium is attained when change of CO_2 into CO+O equals that of CO+O into CO_2 (Dixon and Lowe, Chem. Soc. Trans. 47, 571).

Carbon dioxide is decomposed by the silent electric discharge, the amount of decomposition varying with the degree of dryness of the gas, the intensity of the discharge, and the form of ozoniser employed, but in all cases a diminished pressure of the gas results in a greater decomposition (Holt, Chem. Soc. Proc. 1908, 24, 271).

Ultra-violet light decomposes dry carbon dioxide at the ordinary temperature into carbon monoxide and oxygen; similar results are obtained by the action of radium emanations (Herschfinkel, Compt. rend. 1909, 149, 395; Ramsbottom, Chadwick, and Chapman, Chem. Soc. Proc. 1906, 23).

It is partly changed to carbon monoxide and oxygen by heating to 1300° in a porcelain tube (Deville, Compt. rend. 56, 729; also Berthelot, *ibid.* 68, 1035).

When heated at 350° with hydrogen over reduced nickel or cobalt, it is completely reduced to methane (Sabatier and Senderens, *ibid.* 1902, 134, 689).

With carbon at 500°–650°, it forms carbon monoxide, equilibrium being reached when the mixture of gases contains 61 p.c. unreduced CO_2 (Boudouard, *ibid.* 1899, 128, 824, 1524; 1905, 141, 252).

Mixed with hydrogen and heated to bright redness, or submitted to induction sparks, carbon monoxide and water are formed; if the water is removed, the whole is converted to carbon monoxide (Dixon, Chem. Soc. Trans. 49, 94; Gautier, Bull. Soc. chim. 1906, 35, 929). A mixture of carbon dioxide and hydrogen passed over red-hot pumice yields carbon and water (Dubrunfaut, Compt. rend. 74, 125).

Mixed with sulphur-vapour and passed through a red-hot tube it gives carbon monoxide, sulphur dioxide, and a little carbon oxysulphide (Berthelot, Bull. Soc. chim. [2] 40, 362). Passed through a red-hot tube with sulphuretted hydrogen, it forms carbon monoxide, water, and sulphur (Köhler, *ibid.* 11, 205). Reduced to carbon monoxide by hydrogen, iron, and zinc or copper which has occluded hydrogen (Tissandier, Compt. rend. 74, 531; Schrotter, Wied. Ann. 34, 27); by potassium cyanide (Eiloart, Chem. News, 54, 88); by protoxides of iron and tin (Wagner, Zeitsch. anal. Chem. 1879, 559); and partially by ferrous sulphate, and a little water in a closed tube (Horsford, Ber. 6, 1390).

Carbon dioxide is reduced to carbon by heating with potassium, sodium, magnesium, or silicon (Schmöle, J. Soc. Chem. Ind. 1895, 1060). Alkaline carbonates heated strongly with phosphorus or boron give carbon dioxide, which is reduced to carbon (Tennant, Crelles Annalen, [1793] 1, 158; Dragendorff, J. 1861, 111; Leeds, Bull. Soc. Chim. 12, 1834 and 2131); decomposes moist potassium iodide at high temperatures, yielding hydriodic acid (Papasogli, Gazz. chim. ital. 1881, 227); it also decomposes alkaline aluminates (Ditte, Compt. rend. 1893, 116, 386); and, according to Moore, liberates nitrous acid from nitrites (J. Amer. Chem. Soc. 1904, 26, 959). Solution of carbon dioxide in water yields sodium formate with metallic sodium (Kolbe and Schmidt, Annalen, 119, 251). Carbon dioxide is assimilated by the chlorophyll corpuscles of plants under the influence of sunlight, carbon being abstracted and oxygen set free. Carbon dioxide diffuses through caoutchouc (Kobbe, Chem. Zeit. 1890, 14, 1142).

The specific heat of carbon dioxide is greater at high than at ordinary temperatures (Berthelot and Vieille, Compt. rend. 98, 770 and 852). According to Hoppe-Seyler (Zeitsch. physikal. Chem. 10, 201, and 10, 401), the carbonic acid and marsh gas found in water-logged soils is due to a widespread process of fermentation of cellulose.

In any working- or living-room the carbon dioxide should not be more than 10 volumes per 10,000 of air.

To estimate the carbon dioxide in air, a measured sample of the air is passed through a known quantity of barium hydroxide, coloured with phenolphthalein, and by noting the quantity of air needed to decolourise the hydroxide the carbon dioxide can be calculated. The method is sometimes modified by using a limited volume of air, and titrating the hydroxide remaining unneutralised (Ballo, Ber. 1884, 1097; Wiener, Monatsh. 1894, 15, 429; Henriet, Compt. rend. 1896, 123, 125; Woodman, J. Amer. Chem. Soc. 1903, 25, 150; Jean, Compt. rend. 1902, 135, 746; J. Pharm. Chim. 1903, 27, 418; Pécoul and Levy, J. Soc. Chem. Ind. 1906, 655; Davies and McLellan, *ibid.* 1909, 232).

Carbon dioxide is used extensively in the arts for the manufacture of aërated waters, in sugar manufacture for separating lime from the juice of the sugar-cane, in bread making, and for raising and clarifying beer.

It is also employed for protecting wines from moulds and acetifying organisms. It preserves their aroma and bouquet, and makes the wine fresher, sweeter, and stronger. Wines can also be revivified by the gas (Piaz, J. Soc. Chem. Ind. 1894, 266; 1903, 644; Pini, Bull. de l'Assoc. des Chim. 1898, 15, 741). It also possesses antiseptic properties and retards the putrefaction of meat (Kolbe, J. pr. Chem. [2] 28, 61). It has also been proposed to use it as a motive power where fuel is expensive (Herbert, Chem. Zentr. 1885, 543, 558, 572).

Mixed with acetylene (about 5–8 p.c.), it decreases the smokiness of the flame and prevents the clogging of the burners (J. Gas Lighting, 1898, 72, 916).

Liquid carbon dioxide (Büchner, Zeitsch. physikal. Chem. 1906, 54, 665) can be obtained in large quantities by an apparatus described by Thilorier (Annalen, 30, 122). Natterer compressed carbon dioxide by a specially constructed air-pump (J. pr. Chem. 35, 169; *v.* also Gore, Phil. Trans. 1861, 63). It is prepared from bisulphates by the action of carbonates, the apparatus consisting essentially of a leaden vessel containing a solution of the bisulphate and having a stirring apparatus and gear fixed air-tight to it. By means of a tube and pump an equivalent quantity of calcium carbonate (obtained as a waste product in the manufacture of caustic soda) suspended in water in a second vessel is forced in and the stirrer set in motion. The liberated carbon dioxide is dried and passed into a gasometer from which it is afterwards condensed. An apparatus is also described which allows the evaporation and expansion of liquid carbon dioxide to take place round a tube containing a solution of calcium chloride. The latter is so cooled that it may be used for the manufacture of ice. The carbon dioxide thus used is passed over moist sodium carbonate, converting it into bicarbonate, which may be again used in the carbonic acid manufactory (Thomas, Zeitsch. angew. Chem. 1900, 386). (For description and figure of apparatus for liquifying CO_2 and for bottles in which it is stored and sold, *see* Sisson, J. Soc. Chem. Ind. 1904, 242.)

Liquid carbon dioxide may be bought in iron or steel bottles containing 8 kilos. (about 4000 litres of the gas at ordinary temperature and pressure), costing about 1 sh. per kilo. It furnishes the cheapest means for aërating waters, and is used for raising sunken ships, for driving torpedoes, for extinguishing fires, for cooling purposes, and, as 'Pictet's fluid,' for freezing machines, and by the firm of Krupp, in Essen, for the condensation of steel and other

metals, and is further suggested as a motive power for tramcars and balloons (J. Soc. Chem. Ind. 4, 610).

It is also used for making carbonates and other chemical products for filtering and sterilising organic liquids (d'Arsonval, Compt. rend. 1891, 112, 667), and in Germany for the generation of pressure on storage casks of beer to the faucets above where the beer is drawn for consumption. In Engineering, Dec. 3, 1903, a description is given of its use in railway signalling in outlying stations, to supply the motive power for working the signals, so as to avoid the expense of compression machinery or of long lengths of connecting pipes.

Liquid carbon dioxide is colourless, very soluble in alcohol, ether, and volatile oils, but does not mix with water. When the pressure is suddenly relieved, part of the carbon dioxide immediately vaporises, producing sufficient cold to solidify the remainder. Landolt allows the liquid to evaporate freely into woollen bags, and compresses the solid carbon dioxide in conical wooden moulds by wooden pistons (Ber. 17, 309); *cf.* Purcell (J. Soc. Chem. Ind. 1892, 936; Eng. Pat. 13684, 1891). A vessel for storing solid carbon dioxide is described by Heyl and Wultze (J. Soc. Chem. Ind. 1904, 1215; Eng. Pat. 344957, 1904).

An apparatus for obtaining small and large quantities of solid carbon dioxide is described by Fechlu (J. pr. Chem. 1903, 67, 423; J. Soc. Chem. Ind. 1903, 626); also by Elsworthy (J. Soc. Chem. Ind. 1905, 1231). (For an apparatus for collecting solid carbon dioxide, *v.* Ducretet, Compt. rend. 99, 235.)

Solid carbon dioxide is a white, flocculent, snow-like mass, melting at — 56·7° at 5 atmospheres pressure, and may be left exposed to the air for some time without sensible evaporation. An air or spirit thermometer immersed in it sinks to —79°; it can, however, be placed on the hand without any acute sensation of cold. By mixing with ether its refrigerating power is greatly increased. This is denied by Villard and Jerry (*l.c.*), but the temperature sinks to —85° when it is mixed with chloroform. The temperature can readily be reduced to —90° by passing a current of air through the mixture. At 5 mm. pressure the temperature of solid carbon dioxide soon falls to —125°.

Magnesium powder burnt in a dish of solid CO_2 deposits carbon (Brünner, Ber. 1905, 38, 1432).

Compounds of Carbon.

Carbon tetrabromide or **Tetrabrommethane** CBr_4. White lustrous crystals of a characteristic pungent smell; m.p. 91°; b.p. 189·5° with slight decomposition; b.p. 101° at 50 mm. without decomposition. Occurs in two enantiotropic forms (Rothmund, Zeitsch. physikal. Chem. 1899, 664). Insoluble in water; soluble in alcohol, ether, and chloroform. Best obtained by action of bromine on carbon disulphide in presence of iodine (Bolas and Groves, Chem. Soc. Trans. 1870, 161; 1871, 773).

Carbon tribromide or **Hexabromide**, *Tetrabrommethylene dibromide* C_2Br_6. Small rectangular prisms obtained by action of bromine on ethylene dibromide; or by heating C_2HBr_5 with bromine and water at 170°. Soluble in carbon disulphide; insoluble in alcohol and ether. Decomposed at 200° into C_2Br_4 and Br_2 (Reboul, Annalen, 124, 271).

Carbon dibromide, *Tetrabrommethylene* C_2Br_4. White crystals; m.p. 53°; formed by action of nascent hydrogen on C_2Br_6 (Löwig, Annalen, 3, 292; Lennox, Chem. Soc. Trans. 1862, 14, 209).

Carbon bromide, *Dibromacetylidene* $C:CBr_2$; b.p. 76°. Prepared from tetrabromoethane by removal of two molecules of hydrobromic acid. Spontaneously inflammable in air and very explosive (Lemoult, Bull. Soc. chim. 1905, 43, 193). It contains a double bond (Lawrie, Amer. Chem. J. 1906, 36, 487).

Chlortribrommethane $CClBr_3$. Colourless plates; m.p. 55°; b.p. 160°. Prepared by heating chloroform with bromine at 250°, and retaining fraction distilling at 160° (Besson, Compt. rend. 1892, 114, 223).

Dichlordibrommethane CCl_2Br_2. Fine needles; m.p. 22°; b.p. 135°. Obtained from chloroform by action of bromine as above, retaining the fraction of the product boiling at about 135° (Besson, *l.c.*).

Trichlorbrommethane CCl_3Br; m.p. —21°; b.p. 104°. From chloroform and bromine (Besson, *l.c.*). From bromine and trichloracetic acid (J. H. van't Hoff, Ber. 1877, 678).

Chlorotribromethylene $CClBr:CBr_2$; m.p. 34°; b.p. 203°–205° at 734 mm. (Denzel, *ibid.* 1879, 2208).

***αα*-dichloro-*ββ*-dibromoethylene** $CCl_2:CBr_2$; b.p. 194° (Bourgoin, Bull. Soc. chim. 1875, 116; and Denzel, Annalen, 1879, 208).

***αβ*-dichloro-*αβ*-dibromoethylene** CClBr:CClBr; b.p. 172° at 765 mm. (Swarts, Chem. Zentr. 1899, i. 588).

Trichlorobromoethylene $CCl_2:CClBr$; m.p. —12° to —13°; b.p. 145°–148° (Besson, Compt. rend. 1894, 119, 88).

Chloropentabromoethane C_2ClBr_5; m.p. 170° (Denzel, Ber. 1879, 2207).

***αα*-dichloro-*αβββ*-tetrabromoethane**

$CCl_2Br{\cdot}CBr_3$.

Colourless crystals; m.p. 180° (Denzel, Ber. 1879, 2207).

***αβ*-dichloro-*ααββ*-tetrabromoethane**

$CClBr_2{\cdot}CClBr_2$;

m.p. 191° (Swarts, Chem. Zentr. 1899, [1] 588).

***αββ*-trichloro-*ααβ*-tribromoethane**

$CClBr_2{\cdot}CCl_2Br$;

m.p. 178°–180° (Besson, Compt. rend. 1894, 88).

***αβββ*-tetrachloro-*αα*-dibromoethane**

$CClBr_2{\cdot}CCl_3$.

Prisms from alcohol; smells like camphor. May be sublimed (Paternò, Gazz. chim. ital. 1, 593; Bourgoin, Bull. Soc. chim. [2] 23, 4; Gossner, Chem. Zentr. 1903, ii. 1053).

***ααββ*-tetrachloro-*αβ*-dibromoethane**

$CCl_2Br{\cdot}CCl_2Br$.

Tables from alcohol (Malaguti, Ann. Chim. Phys. 1846, 24; Gossner, Chem. Zentr. 1903, ii. 1053).

Carbon tetrachloride or **Tetrachlormethane** CCl_4 was first obtained by Regnault (Annalen, 1840, [33] 332), who prepared it by the action of chlorine on chloroform in sunshine:

$$CHCl_3 + Cl_2 = HCl + CCl_4.$$

Dumas afterwards obtained it by the action of chlorine upon marsh gas (Annalen, 1840, [33] 187). It can also be prepared by passing carbon disulphide saturated with chlorine through a

red-hot tube. The mixture of carbon tetrachloride and sulphur chloride thus obtained is treated with potash or milk of line and the tetrachloride distilled off (Kolbe, Annalen, 1843, 45, 41; 1845, 54, 146). The tetrachloride may contain carbon disulphide if that substance was in excess, or if the heat was insufficient. This may be removed by leaving the liquid for some time in contact with potash. Geuther removes the carbon disulphide by converting it into potassium xanthate by dissolving the mixture in alcohol, adding alcoholic potash so long as the liquid becomes darker in colour, and heating gently; the unaltered tetrachloride is separated by water and purified by washing (Geuther, Annalen, 1858, 107, 212; and Selmitz-Dumont, Chem. Zentr. 1897, ii. 265).

The complete chlorination of carbon disulphide and of many other carbon compounds can be more readily accomplished in the presence of a chlorine carrier. Thus, in the case of carbon disulphide, bromine has been used (Crump, Chem. News, 1866, 14, 154) and iodine, both alone (Morel, Compt. rend. 1877, 84, 1460) and in the presence of metallic iron (Serra, Chem. Zentr. 1899, ii. 1098); antimony pentachloride reacts with carbon disulphide alone without the addition of chlorine. The mixture becomes hot, and on cooling deposits crystals of antimony trichloride mixed with sulphur, whilst carbon tetrachloride remains in solution (Hofmann, Annalen, 1860, 115, 264).

A large number of other substances can be used as catalytic agents, *e.g.* molybdenum pentachloride (Aronheim, Ber. 1876, 1788), the chlorides of phosphorus and arsenic, and also a series of chlorides of metals, especially those of the iron group. In the presence of these substances, sulphur chloride reacts readily with carbon and excess of chlorine, giving carbon tetrachloride. A stream of chlorine is led over a red-hot mixture of charcoal and sulphur. Carbon disulphide is first formed, then carbon tetrachloride and sulphur monochloride; the latter then breaks up into chlorine and sulphur, and the process begins over again. The carbon tetrachloride prepared in this way is usually contaminated with sulphur chlorides and chlorethane compounds (Combes, Chem. Zentr. 1909, 1, 326; J. Soc. Chem. Ind. 1902, 272 and 1469). In the presence of manganese chloride the reaction can be carried out with precipitation of sulphur, which can be used to manufacture more carbon disulphide (Côte and Pierron, *ibid.* 1903, 962; Febvre, *ibid.* 1905, 1189). Other carbon compounds beside carbon disulphide can be completely chlorinated. Thus chloroform heated with iodine chloride at 165° gives carbon tetrachloride (Friedel and Silva, Bull. Soc. chim. 1872, 537), the same reaction taking place, to a slight extent, in the presence of aluminium trichloride instead of iodine chloride (Monneyrat, *ibid.* 1898, 262).

Perchlormethyl formate, when treated with aluminium chloride in the proportion of 50 parts to 1 of chloride, also yields carbon tetrachloride $CClO_2 \cdot CCl_3 = CCl_4 + CO_2$ (Heutschel, J. pr. Chem. 1877, 306).

The technical preparation of carbon tetrachloride is generally carried out by the direct chlorination of carbon disulphide in the presence of powdered aluminium chloride, the quantity of catalyst necessary being only about 1 p.c. of the carbon disulphide used.

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

The sulphur chloride reacts separately with more carbon disulphide in the presence of iron filings, and the crystalline sulphur which is formed is employed again in the manufacture of carbon disulphide (Urbain, Chem. Zeit. 1902, 1086; Breteau, J. Pharm. Chim. 1908, 110; Urbain, J. Soc. Chem. Ind. 1902, 926; Eng. Pat. 13733).

Later modifications of the process consist in the further chlorination of the sulphur monochloride, in the presence of antimony chloride, before treatment with carbon disulphide (Haworth and Baker, J. Soc. Chem. Ind. 1906, 559), and the use of a solution of sulphur in sulphur monochloride, in a finely divided condition, as a chlorine carrier (Acker and Strue, *ibid.* 1908, 833). Instead of aluminium chloride, aluminium amalgam has been employed (Castner Co. *ibid.* 1905, 903). Under this patent, the resulting carbon tetrachloride is purified by treatment with a solution of alkaline sulphide containing free alkali, the carbon disulphide being removed as thiocarbonate.

A number of electric-heating processes have been suggested. A mixture of sodium chloride and silica is heated in the lowest portion of a furnace lined with magnesia, and provided with three sets of electrodes, one above the other. The middle electrodes heat a mass of coke, and the chlorine from the alkali chloride reacts with the incandescent carbon, forming carbon tetrachloride, which, after passing through the arcs between the third set of electrodes, is distilled off. The temperature does not exceed 2000° (Machalske and Lyon, J. Soc. Chem. Ind. 1903, 1298; Machalske, Chem. Zentr. 1904, 1, 1069). The chlorine can also be supplied from an external source, the carbon only being heated by electricity (Maywald, J. Soc. Chem. Ind. 1907, 1253).

Another process consists in heating together lime, calcium chloride, and carbon in the absence of air in an electric furnace, in the proportions indicated by the equation

$$2CaO + 2CaCl_2 + 10C = 4CaC_2 + 2COCl_2.$$

The carbonyl chloride is led over heated coke, animal charcoal, or pumice, where it is decomposed into carbon tetrachloride and carbon dioxide by surface contact (Machalske and Darlington, J. Soc. Chem. Ind. 1906, 559).

A mixture of calcium chloride and coke, heated in the electric furnace in a stream of chlorine, also yields carbon tetrachloride (Matthews and Darlington, *ibid.* 1906, 1232).

The halogenation of metallic or other carbides, such as acetylene, also yields carbon halides, so long as the temperature is kept below the dissociation point of the halide required (Blackmore, *ibid.* 1908, 712).

Carbon tetrachloride is a transparent colourless liquid, with a pungent aromatic odour; b.p. 76·74°; and sp.gr. 1·63195, 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 201).

The vapour pressure of carbon tetrachloride has been measured by Shreinemakers (Zeitsch. physikal. Chem. 1904, 48, 445). The compressibility has been measured by Richards and Stull (Amer. Chem. J. 1904, 26, 408). In the solid state carbon tetrachloride is trimorphous, the

three modifications melting at −28·6°, −23·77°, and −21·2° respectively, the second being the form usually obtained (Tammann, W. Ann. 1898, 489). The refractive index for the line F is 1·4726, and for the line D is 1·4658 (Gladstone, Chem. Soc. Trans. 1886, 623).

Its dielectric constant has been measured by Turner (Zeitsch. physikal. Chem. 1900, 385), Drude (Zeitsch. physikal. Chem. 23, 267), and Veley (Phil. Mag. [6] 11, 73). Its solubility in water, which is extremely small, has been measured by Rex (Zeitsch. physikal. Chem. 55, 355).

It is soluble in alcohol and ether, and dissolves a large number of organic substances, especially those of a fatty nature, whence its wide application in the arts. It is preferable to carbon disulphide on account of its non-inflammability. With sulphonated oils and resins it yields a gelatinous soap, which is miscible with water (Stockhausen, Chem. Zentr. 1906, ii. 731). It yields chlorine and lower chlorides of carbon on passing through a red-hot tube (Regnault, *l.c.*). When mixed with hydrogen and passed through a red-hot tube with pumice, it yields marsh gas and ethylene (Berthelot, Ann. Chim. Phys. 1858, 53, 69).

The same mixture passed over reduced nickel yields hexachlorethane (carbon trichloride) at 270°. With excess of hydrogen at the same temperature, tetrachlorethylene (carbon dichloride) is obtained (Sabatier and Mailhe, Compt. rend. 1904, 138, 407).

Mixed with sulphuretted hydrogen and passed through a red-hot tube, the vapour of carbon tetrachloride yields hydrochloric acid and carbon sulphochloride $CSCl_2$ (Kolbe, Annalen, 1843, 45, 41, and 1845, 54, 146).

Heated under pressure with oxygen and water at 250°, it forms carbonyl chloride and carbon dioxide (Goldschmidt, Ber. 1881, [14] 928). In alcoholic solution, and treated with potassium amalgam, it yields chloroform, marsh gas, and methylene chloride (Regnault, *l.c.*). Phosphorus pentoxide at 200° acts in two ways: in the first, carbonyl chloride and carbon dioxide are produced; in the second, in the presence of more phosphorus pentoxide, carbon dioxide alone is obtained.

$$2CCl_4+P_2O_5=COCl_2+CO_2+2POCl_3$$
$$3CCl_4+2P_2O_5=3CO_2+4POCl_3$$

(Gustavson, Zeitsch. f. Chem. 1871, 615).

A similar reaction takes place at 100° with sulphur trioxide, carbonyl chloride being formed:

$$CCl_4+2SO_3=S_2Cl_2O_5+COCl_2$$

(Erdmann, Ber. 1893, 26, 1993).

With the oxides of many metals, a similar production of carbonyl chloride, together with carbon dioxide and the chloride of the metal, takes place (Demarcay, Compt. rend. 1887, 104, 111; Quantin, *ibid.* 1887, 104, 223; 1888, 106, 1074; Delafontaine and Linebarger, Amer. Chem. J. 1896, 532).

With zinc and dilute acid, carbon tetrachloride is converted into hydrochloric acid and chloroform (Geuther, *l.c.*). Alcoholic potash slowly converts it into potassium chloride and carbonate (Regnault, *l.c.*). By long-continued action at 100° in sealed tubes, alcoholic potash converts it partially into ethylene (Berthelot, Ann. Chim. Phys. 1859, 109, 118). With alcoholic potash and aniline it yields phenyl*iso*cyanide (*cf. Chloroform*). With phenylamine it yields carbotriphenyltriamine (Hofmann, Proc. Roy. Soc. 9, 284, and 10, 184). By the action of sulphur at 220°, a number of sulphochlorides of carbon are formed, the final product being carbon disulphide (Klason, Ber. 1887, 20, 2376). It is decomposed at 200° by molecular silver, being converted into hexachlorethane C_2Cl_6 (Goldschmidt, Ber. 1881, 14, 927). By heating with aluminium bromide it is readily converted into carbon tetrabromide (Gustavson, Bull. Soc. chim. 1881, 556).

Heated in a sealed tube for 10 hours at 130° with hydriodic acid, carbon tetrachloride yields iodoform and hydrochloric acid (Walfisz, *ibid.* 1893, 7, 256). Acetylene reacts with carbon tetrachloride, yielding free carbon in a very finely divided form, hydrochloric acid being formed at the same time (Sandman, Chem. Soc. Abstr. 1902, 82, i. 581). Carbon tetrachloride reacts with benzene in the presence of aluminium trichloride, giving, as chief product, diphenyldichloromethane, $CCl_2(C_6H_5)_2$ (Böeseken, Chem. Soc. Abstr. 94, i. 189).

In its physiological action, carbon tetrachloride strongly resembles chloroform.

Its popularity as a solvent in the arts has been somewhat diminished by the increasing manufacture of tetrachlorethane $C_2Cl_4H_2$, as the latter is more indifferent toward metals, and is readily produced by the action of chlorine on a double compound of antimony pentachloride and acetylene (D. R. P. 154657, 1906).

Carbon trichloride, *Carbon hexachloride, Tetrachlorethylene dichloride, Hexachlorethane, Perchlorethane* C_2Cl_6, discovered by Faraday (Phil. Trans. 1821, 47); also investigated by Regnault (Ann. Chim. Phys. 1838, [2] 69, 166, and 1839, [2] 71, 371). Is obtained by the action of chlorine in sunshine upon various derivatives of ethyl and ethylene; on carbon dichloride; on ethylene chloride (Faraday, *l.c.*); and also (Liebig. Annalen, 1, 219) on ethyl chloride, first in the shade, afterwards in sunshine (Laurent, Ann. Chim. Phys. 1837, [2] 64, 328); on mono-, di-, or tri-chlorinated ethyl chloride (Regnault, *l.c.*); on ethyl sulphite (Ebelmen and Bouquet, *ibid.* 1846, [3] 17, 66); on ethyl oxide (Regnault); on hydrochloride of ethylamine (Geuther and Hofacker, Annalen, 1858, 108, 51) (in this process some chloride of nitrogen is produced); by passing the tetrachloride through a red-hot tube (Kolbe, Annalen, 1845, 54, 147); by distilling perchlorethylic oxide, and repeatedly treating the distillate with water (Malaguti, Ann. Chim. Phys. 1846, [3] 16, 14); by heating carbon tetrachloride with copper powder at 120° (Radziszewski, Ber. 1887, 17, 834) or with molecular silver at 200° (Goldschmidt, *ibid.* 1881, 14, 928); by heating acetyl chloride with excess of phosphorus pentachloride at 180° (Hübner and Müller, Zeitsch. f. Chem. 1870, 328); by heating propyl chloride or *iso*butyl chloride with iodine trichloride at 200° (Krafft and Merz, Ber. 1875, 8, 1298); by treating pentachlorethylchloroformic ester with aluminium chloride (Müller, Annalen, 1890, 258, 63).

Carbon trichloride crystallises from a mixture of alcohol and ether in right rhombic prisms (Gossner, Chem. Zentr. 1903, ii. 1052). Colourless, transparent, and nearly tasteless, but having

an aromatic odour resembling that of camphor; sp.gr. 2·0; m.p. 184°–186° (Bolton, Zeitsch. Elektrochem. 1902, 8, 165; 1903, 9, 209), volatilising even at ordinary temperatures; b.p. 185° (Hahn, Ber. 1878, 11, 1735). Insoluble in water; soluble in alcohol and ether, and in all oils. Converted, by repeated distillation, into the dichloride and free chlorine. Burns with a red light in the flame of a spirit lamp. Mixed with hydrogen and passed through a red-hot tube, it yields dichloride and hydrochloric acid (Geuther, *l.c.*). Metals heated in its vapour form metallic chlorides, charcoal being deposited. Heated in sealed tubes with potassium hydroxide, it yields potassium oxalate and chloride

$$C_2Cl_6+8KHO=K_2C_2O_4+6KCl+4H_2O$$

(Geuther, J. 1859, 277). The same products together with hydrogen and ethylene are formed when it is heated with alcoholic potash in sealed tubes (Berthelot, Annalen, 1859, 109, 118).

Reducing agents, such as zinc and dilute sulphuric acid, or alcoholic potassium hydrogen sulphide (Regnault, *l.c.*), reduce it to tetrachlorethylene (carbon dichloride). The same reaction takes place when it is heated with silver at 280°. Sulphur trioxide acts upon it at 150° according to the equation

$$CCl_3{\cdot}CCl_3+2SO_3=CCl_3{\cdot}COCl+S_2O_5Cl_2$$

(Prudhomme, Annalen, 1870, 156, 342).

Carbon dichloride, *Tetrachlorethylene* C_2Cl_4 (Faraday, Phil. Trans. 1821, 47; Regnault, Ann. Chim. Phys. 1839, [2] 70; [2] 71, 372), is formed as a liquid coloured with chlorine when the vapour of carbon trichloride is passed through a red-hot tube filled with fragments of glass. It is purified by passing it repeatedly through a red-hot tube, then shaking up with mercury and rectifying at a low temperature (Faraday). More easily obtained by adding carbon trichloride in small portions to an alcoholic solution of hydrogen potassium sulphide, as long as sulphuretted hydrogen is given off. The liquid is distilled and carbon dichloride separates from the distillate on dilution with water (Regnault, *l.c.*); or by reduction of carbon trichloride with zinc and sulphuric acid. Mobile liquid of sp.gr. 1·619 at 20° (Regnault), 1·612 at 10° (Geuther); b.p. 122° (Regnault), 116° (Geuther); remains liquid at −18°, and does not conduct electricity. Insoluble in water, acids, and alkalis, but dissolves in alcohol and ether, and oils. Decomposed at a red heat into the *hexchlorobenzene* C_6Cl_6 and free chlorine. When its vapour is passed over baryta at a red heat, it is decomposed with vivid ignition into barium chloride, carbon dioxide, and charcoal. It absorbs bromine in the sunshine, forming *carbon chlorobromide* $C_2Cl_4Br_2$. It is converted by continued heating to 200° with potassium hydroxide into potassium oxalate and chloride, hydrogen being given off (Geuther, Annalen, 247). It absorbs dry chlorine in sunshine, forming the trichloride, but is converted into *trichloracetic acid* when exposed to an atmosphere of chlorine under water

$$C_2Cl_4+2H_2O+Cl_2=3HCl+C_2HCl_3O_2$$

(Kolbe, Annalen, 1845, 54, 181).

Hexchlorobenzene C_6Cl_6; m.p. 225°; discovered in 1821 by Julin and investigated by Phillips and Faraday (Phil. Trans. 1821), and by Regnault (Ann. Chim. Phys. [2] 70, 144), who prepared it by passing the vapour of chloroform or tetrachlorethylene through a porcelain tube filled with fragments of porcelain and heated to redness. Obtained from methylene chloride by ICl or ICl_3 (Höland, Annalen, 240, 234); the crystalline product is dissolved in ether, filtered, evaporated to dryness, and sublimed. Obtained by Hugo Müller as a final product of the action of antimony pentachloride or chlorine in presence of iodine on benzene. It is also obtained by sending a current of 5·5 amperes and 42 volts for ½ hour between carbon electrodes in an atmosphere of chlorine. If a higher current and voltage are used, and it is continued for much longer, the trichloride C_2Cl_6 is formed. Bromine yields similar compounds (Bolton, *l.c.*). Forms white delicate needles with a silky lustre, tasteless, but with an odour resembling spermaceti; sublimes without fusion at 120°.

Insoluble in water, acids, and alkalis, but soluble in alcohol, ether, and hot oil of turpentine. Decomposed into chlorine and charcoal on passing through a red-hot porcelain tube filled with glass or rock crystal. Burns with a bluish colour in the flame. Potassium burns on being strongly heated in its vapour. Formerly regarded as carbon monochloride: molecular formula established by Bassett (Chem. Soc. Trans. [2] 5, 443).

Carbon tetraiodide, *Tetraiodomethane* CI_4. Dark-red octahedra; sp.gr. 4·32; obtained by action of aluminium iodide on a mixture of carbon tetrachloride and disulphide (Gustavson, Ber. 14, 1705).

Carbon nitride (*v. Cyanogen*, art. CYANIDES).

Carbon subnitride C_4N_2 has been obtained by Moureu and Bougrand (Compt. rend. 1910, 150, 225) by removing two molecules of water from the diamide of acetylene dicarboxylic acid. $CONH_2{\cdot}C:C{\cdot}CONH_2=N:C{\cdot}C:C{\cdot}C:N+2H_2O$. It forms fine white needles; m.p. 20·5°–21°; b.p. 76° at 753 mm., and its vapour has an odour and an irritating action resembling that of cyanogen. It is readily combustible, and takes fire spontaneously at 130°, burning with a purple flame, also resembling that of cyanogen. It has an abnormally high molecular refraction and dispersion, and a density of 0·9703 at 25°/4°.

Carbon oxychloride $COCl_2$, *Carbonyl dichloride, Chlorocarbonic acid, Phosgene gas.* First obtained by J. Davy by action of sunlight on mixture of carbon monoxide and chlorine. (For details of this mode of preparing it, *v.* Emmeling and Lengyel, Annalen Suppl. 7, 101, and Wilm and Wischin, *ibid.* 147, 450.) Also obtained by passing carbon monoxide into boiling antimony pentachloride (Hofmann, *ibid.* 70, 139; Butlerow, Zeitsch. f. Chem. 1863, 484; Kraut, Gm.-K. I. 2, 380); by heating carbon tetrachloride with zinc oxide in closed tubes at 200°, or by mutual action of carbon tetrachloride and carbon monoxide at 400°; or by heating a mixture of chloroform, potasssium dichromate, and sulphuric acid.

Carbon oxychloride is a colourless liquid, boiling at 8·2°, and of sp.gr. 1·432 0/4°. Soluble in acetic acid and benzene; decomposed by water: $COCl_2+H_2O=CO_2+2HCl$. With alcohol forms *chlorocarbonic ester* $Cl{\cdot}COOC_2H_5$. Combines with ammonia to form *urea* and ammonium chloride.

Carbon disulphide, *Thiocarbonic anhydride, Sulphocarbonic acid* CS_2. This compound was discovered by Lampadius, in 1796, by heating pyrites with charcoal. Clement and Desormes, in 1802, in examining the action of sulphur on red-hot charcoal, obtained the same product. Its nature was established by Vauquelin.

Manufacture.—Schrötter in Germany, and Peroncel in France, first prepared carbon disulphide on a manufacturing scale. Schrötter employed a cylinder of Hessian clay in which the charcoal was heated; the sulphur was introduced through a hole near the bottom, to the upper end was fixed an exit tube for the vapour of the carbon disulphide formed. The apparatus produced about 20 kilos. of the disulphide in 12 hours.

Deiss and Fisher employed cast-iron cylinders in which the vapour of sulphur passed over charcoal heated to redness. Fireclay retorts glazed internally to prevent the escape of vapour through the pores were also used, each cylinder was about 5 feet high and nearly 20 inches diameter. Four retorts were arranged in a single furnace in such a way that the flame of the fire could play entirely round them. Each retort was divided internally into two parts by means of a perforated shelf; the upper compartment, which was the larger of the two, served to contain the charcoal, which could be thrown in through a special opening in the lid without interrupting the working. A second opening in the top of the retort was provided with a tube about 2 inches in diameter, which led directly into the lower compartment, and was used to throw in sulphur as required. The vapour of carbon disulphide which was formed during the process was conducted through a delivery pipe connected with a third opening in the retort into the condensers. The four retorts, having been filled with charcoal and the lids closed, were heated to redness by a coal fire. Pieces of sulphur wrapped in cylindrical paper packets were then dropped in the pipes leading to the lower partitions of the retorts. Two such packets, each containing about 5½ oz. of sulphur, were thrown in at intervals of about 3 minutes, the opening at the end of each tube being closed at each successive addition. The charcoal was renewed every 7 hours, and was heated about an hour and three-quarters each time before the necessary temperature was attained for its combination with sulphur. The vapour of carbon disulphide mixed with that of sulphur escaped through the delivery tubes, passing into the first row of condensers, where it was partially condensed, together with some sulphur; the undissolved sulphur was recovered and used over again. Thence the uncondensed vapours passed on into the second row of condensers, and so on till the last row. The condensers, amounting to 18 or 20 in all, were connected together by pipes, the last of which was connected with the chimney of the works, or better, with vessels or tubes containing layers of pulverised lime to absorb the sulphuretted hydrogen which would otherwise create a nuisance in the neighbourhood of the factory.

The condensers were made of sheet zinc, were cylindrical in shape and about 26 inches in diameter, bottomless, with slotted sides, and stood in a kind of shallow cistern containing water a little deeper than the openings, so as to form a water lute, permitting the passage of the condensed liquid while closing the exit against vapours. The lids of these condensers were furnished with rims forming a kind of saucer, containing water to assist in the condensation of the vapour. Each lid had two openin s in the form of tubulures, into which the pipes were fixed for the transmission of the vapours from condenser to condenser.

Gérard employed a vessel of cast iron 6½ feet in height, about 4 feet 8 inches in diameter, and sides

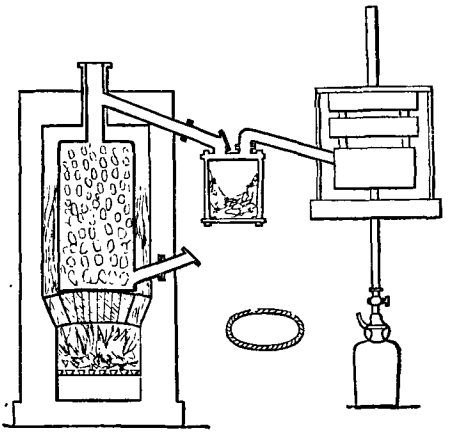


Fig. 15.

1¾ inch thick (Fig. 15). The retort was elliptical in section, stood upon a brickwork arch, and was heated from below by a fire. Near the bottom was a pipe fitted with a valve, through which sulphur could be introduced into the cylinder. At the upper extremity was a wide pipe which could be closed with a lid, and served for the introduction of charcoal into the apparatus. Another pipe, cast in one piece with the upper one, sloped forward and passed into a receiver in which the sulphur which passed over during the operation was condensed, and could be easily removed by opening a valve in a tubulus placed at a bend in the pipe; the more volatile carbon disulphide passed forward into the condensers. The condenser consisted of three vessels, cylindrical in form, arranged one above the other, and communicating by vertical pipes. The topmost condenser had an exit pipe for sulphuretted hydrogen, &c., and the condensed carbon disulphide could be drawn off into a receiving vessel beneath by opening a cock in a pipe proceeding from the lower condenser.

The three condensers were contained in a tank 5 feet high and 5 feet wide, filled with water, which could be renewed at pleasure.

The sulphur was added in portions of about 3 lbs. at intervals of 3 minutes. The oven was heated during the night to volatilise the sulphur, and the residual charcoal was added to the new charge. This apparatus yielded in 24 hours about 570 lbs. of carbon disulphide, consisting theoretically of 480 lbs. of sulphur and 90 lbs. of carbon; in practice 530 lbs. of sulphur and 242 lbs. of wood charcoal were used. Gérard found it advantageous to surround the generating

vessels with brickwork, which rendered them more durable.

Only retorts of a certain size could be employed, as, when they were too large, the heating was irregular, causing waste of sulphur. When using unrefined sulphur, the retorts needed cleaning every fortnight, but with purified sulphur they could be kept working for two months.

The present mode of manufacture is thus described by Ignatius Singer (J. Soc. Chem. Ind. 8, 1889, 93) (see Fig. 16):

A is a vertical cast-iron retort, or, better still, made of earthenware, glazed inside, of elliptical shape, about 66 inches high, and 20 by 12 inches internal diameter. It rests on a support, B, made of firebricks, and is protected by a mantle of best firebricks, C, about 4 inches thick, leaving a space of from $\frac{1}{2}$ to $\frac{3}{4}$ inch between it and the retort. The metal of the retort should not be less than 2 inches in thickness. D is the outer brickwork of the furnace lined on the inside with firebricks, D'; E, E, fire-grates; E', ash pits; F, furnace doors, made of frames, *a*, into which a fire-proof slab, *b*, is inserted. The furnace doors are suspended by cables running over pulleys, and are counterpoised, so that they can be raised or lowered. At *d* is shown a small peep-hole, through which the temperature in the furnace may be watched. In the lid of the retort are cast two tubes, G and G', of about 5 inches internal diameter and not less than 1 inch in thickness, but it is advisable to have them made somewhat stronger, as the lid will then outlast several retorts. Over the openings, G, a vent-pipe or flue, H, is suspended by a lever, so that it can be raised or lowered at will, one end of which passes through the roof. When fresh charges of charcoal are to be introduced into the generator A, which is done through the tubulure G', the lid closing the tube G is first removed, and the vent-pipe H quickly lowered, which serves the purpose of carrying off the noxious gases that would otherwise be injurious to the workmen. G' may now be opened, and the carbon fed in without the slightest inconvenience.

From the tubulure G' issues a pipe, I, inclined upwards, through which the disulphide of carbon vapours escape. Most of the free sulphur passing over will condense here and run back into the retort. But the partially cooled sulphur falling on to the surface of the incandescent carbon would be immediately vapourised again, at the same time cooling down the top layer of the charcoal. To obviate this, Singer suggests than an opening should be made in the lower part of the pipe I, to which a hopper can be fitted, as shown at J, terminating in an earthenware pipe K, reaching nearly to the bottom of the retort. By this means the sulphur distilling over uncombined would be conducted back to the bottom of the generator, the pipes would be less liable to be choked up, while the resulting product would be purer.

From the lower end of the retort, close to the bottom, a pipe M branches off, a little upwards inclined, passing through the brickwork and terminating in a chamber N, with door *n*. During work this pipe is carefully closed by a lid. It serves the purpose of raking the ashes out of the retort, which is done once a week. At *m* a flue is shown, carrying the noxious gases into the chimney. The ashes are allowed to cool here before their removal. Adjoining this chamber is a hearth into which an iron vessel, O, is fitted, for melting the sulphur. It is heated by a flue from the furnace passing underneath it, provided with a damper to regulate the heat. (In Fig. 16 this sulphur vessel is raised so as to make it visible in the drawing.) A pipe, *o*, closed by a conical valve to which an iron rod, *o'*, is attached, connects the sulphur pot with the arm M of the retort, by which means the sulphur can conveniently be introduced into the latter.

The sulphur flowing down the incline of the arm M arrives at the bottom of the retort, where it is volatilised; the vapours, passing upwards, combine with the carbon. The generated disulphide vapours escape through pipe I, and then pass down the vertical tube I' into a vessel P, where any excess of sulphur is deposited. The lid of this vessel rests in hydraulic seals, and is connected with the inlet and outlet pipes by a kind of telescopic tube made air-tight by water. When the vessel P is to be removed, the lid is raised, the vessel taken away, another similar one put in its place, and the lid lowered again. This should be done once a week only, and never while distillation is going on.

The carbon disulphide vapours, now freed from the greater part of uncombined sulphur, pass through a Liebig's condenser, L, about 30 feet long, into a receiver, S, partially filled with water. The crosspiece T, connecting the Liebig's condenser with the receiver, is made so that it can be detached—being secured at *v* by flanges bolted together, and at v^1 by water seal—for purposes of cleaning, &c. From here the disulphide is allowed to run through a siphon, *p*, direct to the storage tanks. A better plan, however, is to keep the storage tanks for the crude product on a high level, which greatly facilitates the after-process of purification. In this case the disulphide of carbon is allowed to flow into a *montejus*, U, as shown in drawing, A pipe *q*, reaching nearly to the bottom, is passed through the cover of the *montejus* to the high-level tank. A second pipe, *r*, connects the vessel U with a force-pump. On air being pumped into U through *r*, the stop-cocks p^1 and p^2 having been shut off, the disulphide is pressed up through pipe *q* into the tank. This is a far better method than using pumps, as in the latter it is difficult to prevent leakage, the crude disulphide having a very corrosive action on most metals. For the same reason, the receivers, tanks, &c., for the crude substance should all be lined with sheet-lead, as wrought-iron vessels soon perish, while copper is even more energetically acted upon. Cast iron withstands corrosion much better, but is objectionable on account of its porosity. This might be remedied, however, by giving the vessels repeated coatings of dilute silicate of soda, both inside and outside, the vessels being first slightly heated with steam and the silicate applied while warm.

Near to the top of the receiver S is a pipe, *s*, for carrying off the uncondensable vapours—chiefly sulphuretted hydrogen. The gases are, conducted into a rectangular vessel, W, where they are made to circulate in zigzag over a series of shallow trays filled with a vegetable oil, to

absorb any disulphide vapours which have escaped condensation. The oil can be made to trickle from a reservoir, *x*, as shown, through a goose-necked pipe, which, passing from tray to tray in an opposite course to that of the gases, finally trickles through *x* into a receiver, Y. When a sufficient quantity has accumulated here, the disulphide is distilled off and the oil returned to *x*. Before the gases enter this absorber they are 'washed' by making the end of the pipe *s* dip into the oil as shown at *y* whereby the apparatus is disconnected from contact with air. The gases are now passed through a second vessel, Z, similar in construction to the one just described, only substituting lime or oxide of iron for the oil, to absorb the H_2S, and are then allowed to escape into the open air through the pipe *z*.

Above the retort A, and between it and the chimney, set at right angles to each other, is a smaller retort, similar in construction to A, but only about one-third the capacity of the latter, and is heated by causing the products of combustion coming from the furnace to circulate round it before finally passing into the chimney. (Only the discharge hole *h'*, corresponding to the arm *m* of the retort A, is visible in the drawing.)

As the generator A requires fresh charges of carbon every 8 hours, it is very economical to keep this small retort always filled with charcoal, which by the time it is required will be red hot, and no more time need be lost than is required for transferring it from the one into the other retort. By this arrangement, part of what would otherwise be waste heat is utilised, and a great saving in time and fuel effected. A still better plan is to make the charcoal on the spot, 8 hours being more than sufficient to char the wood and to heat it up to bright redness. Spent dyewoods, tanner's refuse, or sawdust, are excellent for the purpose, and as these would not require crushing—as when charcoal is bought in lumps—a saving in labour, possibly also in money, might be made, besides being more cleanly. By a small outlay, the vapours might be condensed, and pyroligneous acid obtained as a by-product.

The apparatus is worked as follows: After having allowed the brickwork to set and partially dry for a few days, the fires are started, at first gently, to prevent the brickwork from cracking, then gradually increasing the heat until the retort becomes a dull-red colour. The latter is

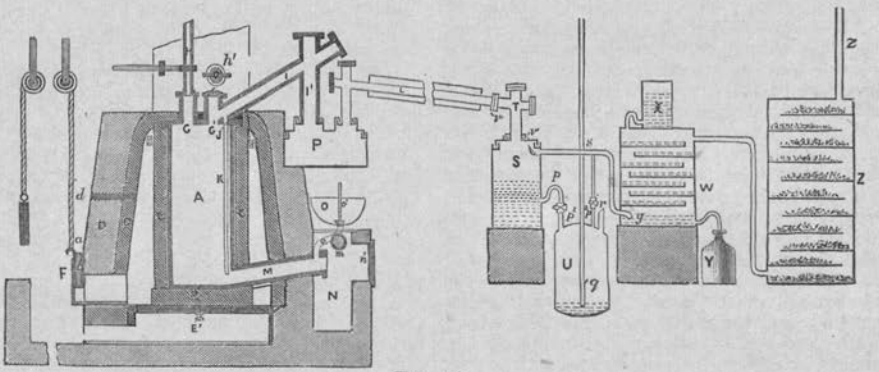


FIG. 16.

now filled with small charcoal, and the smaller retort with chips, sawdust, &c., and the fires are now urged until the retort and the charcoal in it have become a 'cherry red.' This heat should never be exceeded, nor should it be allowed to fall below this, as in either case it would result in a lesser yield of carbon disulphide.

When the proper temperature is attained, the two openings in the lid of the retort are closed, the lids being screwed down tightly, with some clay made into a thick paste as a lute. A better way would be to cast in the top of these tubulures grooves, and the lids with a rim loosely fitting into these grooves, forming what is called an hydraulic seal, only using lead in the place of water. The heat there is sufficient to melt lead, but not so great as to prevent its use. This would form a much better lute, and could be opened and closed in much less time, which, in the case of disulphide of carbon manufacture, is a great desideratum. Having previously secured all the joints throughout the apparatus, sulphur is now run in by raising the rod *o'* in the sulphur pot. A bubbling will immediately be heard in the gas washer at *y*, caused by the escape of sulphuretted hydrogen, &c. In a few minutes, this bubbling ceases, and carbon disulphide begins to distil over. Distillation is now proceeding, sulphur being charged in every 5 minutes, about 1½ to 1¾ lbs. each time, for 7 hours, when the supply of sulphur is stopped, and one hour allowed to elapse before fresh charcoal is filled in. The lid is then removed from C, and the flue-pipe H lowered. C' may now be opened, and last of all the lid *h'* is removed from *h* of the carboniser, and the red-hot charcoal raked from the carboniser, by means of a funnel or hopper, into the retort A. The retort is now closed, taking care that the opening communicating with the flue H is the last to be shut off, and work started again. At the end of each week, neither coal nor sulphur is charged in for 8 hours, after which the whole apparatus is cleaned out in the following manner: The flue H having been lowered on to G as described above, the cover at the end of the delivery pipe I is removed, and wet bags or pieces of canvas are tightly rammed down the pipe I, and past its junction with the vertical pipe I', so as to isolate the condensers, &c., from the furnace. The ashes are now raked out through M, as described above, the retort refilled with fresh charcoal,

and while this is getting heated up, the other portions of the apparatus are examined, and where sulphur is present it is removed.

With one such retort, from 4 to 5 cwts. of carbon disulphide can be made in a day, but it is much more economical, both in labour and fuel, to have several retorts—say four—in the same furnace.

Manufacture of Carbon Disulphide by the Electric Furnace.

Carbon disulphide is now made on the large scale, near Penn Yan, N.Y., America, by the Taylor Chemical Company, by means of an electric furnace, devised and patented by Mr. Edward R. Taylor (U.S. Pat. 688364, Dec. 10, 1901; 871971, Nov. 26, 1907), who has kindly supplied the information upon which the following description of the process is based. The construction of the furnace is shown in Figs. 17, 18, 19, 20, 21. Fig. 17 shows a section in elevation

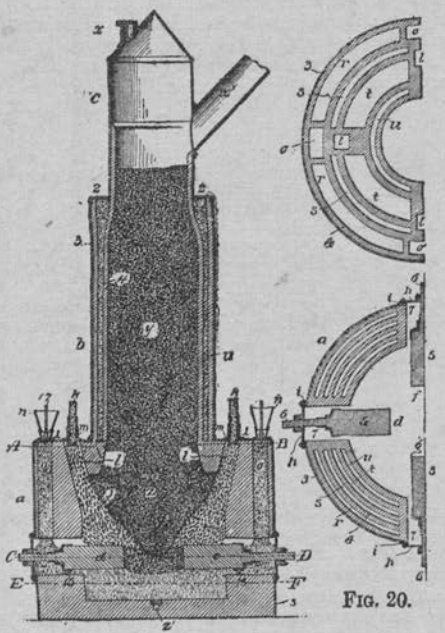


Fig. 17.

Fig. 20.

through the electrodes, and Fig. 18 shows a cross section in elevation at right angles, the figures being taken from the patent specifications. In Fig. 17 is shown the position of the electrodes *d*, D, near the bottom of the furnace shaft, which is represented as filled with charcoal; in Fig. 18, they are seen at *d*. At *k* (Fig. 17) are pipes through which are passed broken carbons, *i.e.* refuse from the factories of carbons for arc lights, for the purpose of reinforcing the main carbons; these pass down, upon, and over the ends of the main carbons, and convey the current from the electrodes to the charcoal. The intermediate conductive material protects the electrodes proper from the intense heat and eroding action and thereby prolongs their life. It also tends to steady the current, fluctuations being mainly due to variations in power and not to changes of resistance in the furnace itself. The charcoal for the reaction is fed into the furnace through the opening *x* (Fig. 17). Preferably four electrodes are used in this construction, supplied with two-phase alternating current. Provision is made for keeping the metallic portions of them comparatively cool by feeding cold sulphur on to them through the inlets shown as *o* (Fig. 17), and which can be replenished through the hoppers *n*, the sulphur passing into the annular chambers shown below the hoppers, seen in detail in Figs. 19, 20, and 21. The interior of the furnace thus filled with sulphur, which is gradually melted and finds its way to the reaction zone. By this construction, the heat that would otherwise be radiated from the external walls of the furnace is absorbed, and no outside lagging is needed. The furnace is 16 feet in diameter and 41 feet high. It needs much less care and is easier to manage than one of the small iron or clay retorts generally used.

In working, charcoal is put into the charger above the bell and the opening sealed. The charcoal falls into the shaft of the furnace as

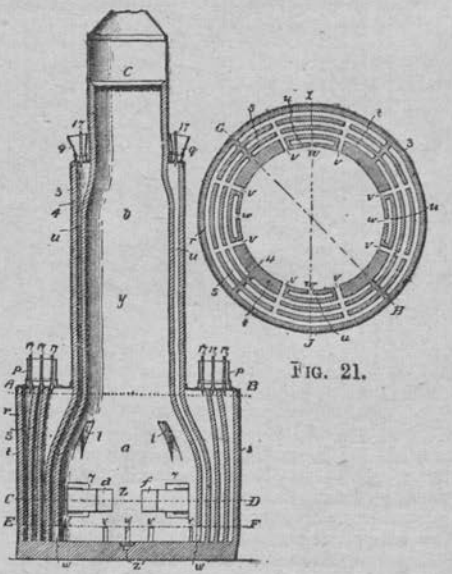


Fig. 21.

Fig. 18.

often as there is room for it, the charger being replenished from time to time. The shaft should be kept filled with charcoal and the internal spaces filled with sulphur: thus there is no loss of heat by radiation and the heat absorbed in melting the sulphur is returned to the furnace.

Electricity is supplied in such quantity that the electrodes are not submerged in the melted sulphur to such an extent as to restrict the passage of the current. The electricity is ordinarily passed from the one electrode to the other immediately opposite, but the direction can be changed at any time so as to pass to the adjacent electrode, thus burning out any piers or 'scaffolds' that may form in the corners and which would prevent the regular descent of the charge. The sulphur within the working

chamber z soon becomes melted, and its level rises more or less nearly to the top of the electrodes. As it approaches the heat zone, the sulphur is vapourised and rises through the charcoal which, when sufficiently heated, combines with it, forming the disulphide, the vapour of which ascends through the charcoal in the shaft, and passes out through the pipe *x*, to a condenser. The furnaces are run for about a year before renewing the electrodes or cleaning out. Aluminium bars, 6 inches wide and

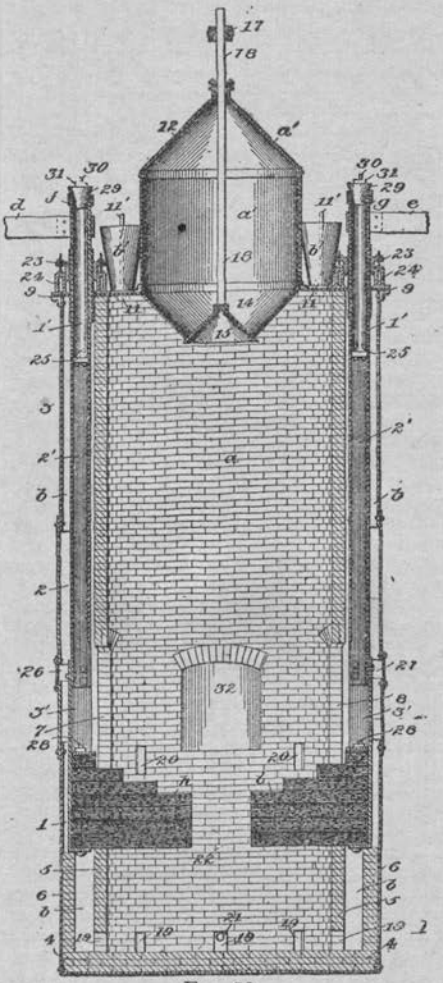


FIG. 22.

⅝ inch thick, connect the insulated electrodes with two Stanley inductive type dynamos, each of 330 kilowatts capacity, run, as a rule, by water power. The average voltage is about 50. The yield is usually about 14,000 lbs. of the disulphide in 24 hours, but it is capable of being increased to 25,000 lbs.

An improved type of electric furnace, more particularly adapted for a smaller installation, is seen in Figs. 22 and 23, reproduced from the patent specifications.

Fig. 22 shows the furnace in sectional elevation. Fig. 23 shows a sectional elevation with the plane of the section at right angles to that of Fig. 22, and with portions broken away at top to expose parts behind the plane of the section. Fig. 24 is a top view on which the planes of Figs. 22 and 23 respectively are indicated by broken lines, A–B and C–D; and Fig. 25 represents a horizontal section on the line E–F

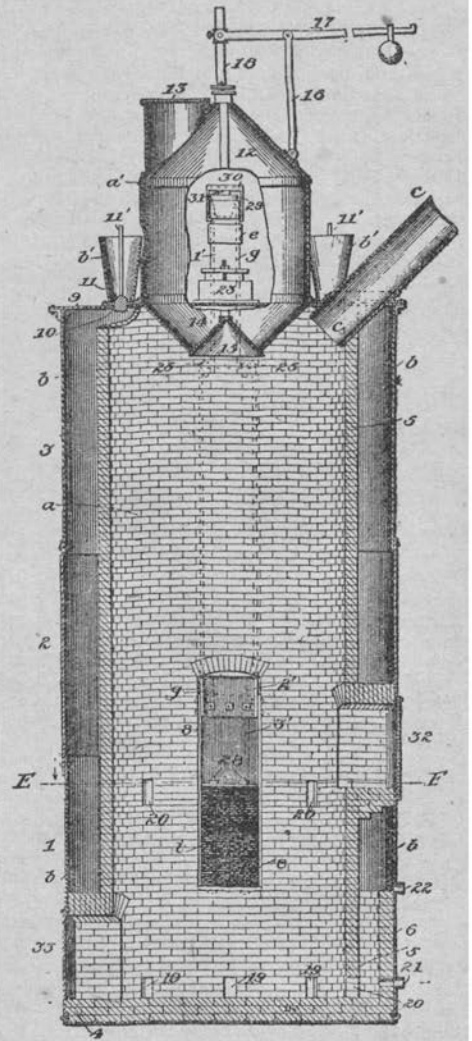


FIG. 23.

(Fig. 23). Like reference characters refer to like parts in all the figures. There is an outer shell of iron or steel within which, at the bottom, is a flat hearth of floor 4 (Figs. 22, 23, and 25) of firebrick, which supports a circular wall of like material, within which is the working chamber *a* of the furnace, and an outer wall, 6, concentric with the wall 5, extending upward a short distance and terminating substantially on a level with the bolster, forming lower ends of a pair of diametrically opposite embrasures, 7 and 8.

The wall 5 of the working chamber *a* is continued upward to the top of the outer shell 1, 2, 3; a feed chamber *b* for sulphur being formed between the walls 5 and 6 at bottom and between the wall 5 of the working chamber and the outer shell above the top of the outer wall 6.

The shell 1, 2, 3 terminates at top in a horizontal annular top portion, 9 (Figs. 22, 23, 24),

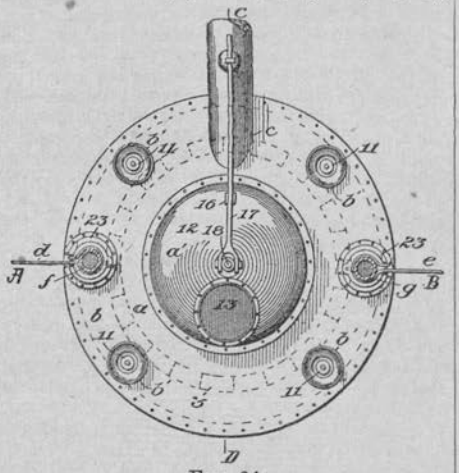


FIG. 24.

which is provided at suitable intervals with hoppers *b'* and with openings 10 (Fig. 23) at their bottoms, communicating with said feed space *b*, each of the hoppers being provided with a suitable plug, 11, having a handle, 11', extending above the top of the hopper, so that the hoppers may be filled above the plugs, and the plugs then lifted to drop the contents of the hoppers into the feed space *b*, and quickly replaced to prevent the escape of fumes and the admission of air.

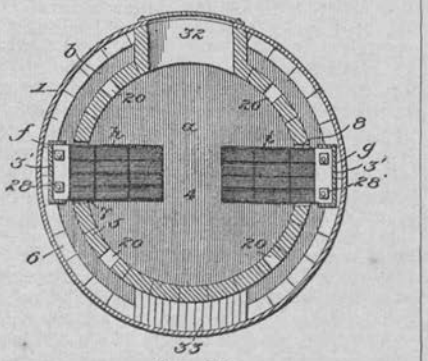


FIG. 25.

Within the central opening of the top portion 9, of the shell, a charcoal hopper, *a'* (Figs. 22, 23, 24), is supported: this is constructed with a conical top, 12, provided with a capped charging neck, 13, through which the charcoal is introduced into the hopper, and a conical bottom, 14, depending within the upper end of the working chamber and provided with a central opening closed by a bell, 15; the top of the hopper being further provided with the supporting link 16 of a weighted lever, 17, connected with the said bell 15, by a rod, 18, and rendering the hopper *a'* normally closed at bottom. A discharge pipe, *c* (Figs. 23 and 24), extends from the working chamber *a* through the top portion 9 of the shell, in an oblique direction, as shown in Fig. 23.

Openings 19 and 20 (Figs. 22, 23, and 25) for the sulphur, are formed in the working chamber wall 5, immediately above the floor 4, and at one or more higher points, connecting the feed space *b* with the working chamber *a*, and pipe openings 21 and 22 extend through the outer wall 6 and the lower shell section 1 at different heights to allow the sulphur to enter the furnace proper. Metallic conductors, *d* and *e* (Figs. 22 and 24), connected with the source of electricity, are attached respectively to the protruding upper ends of metallic electrode stems *f* and *g*, which extend to the top of the outer wall 6, and rest upon the top of this wall, as in Fig. 22. Each of the electrode stems *d* and *e* is made in three sections, numbered respectively, 1', 2', and 3' in Fig. 22; the upper section 1' of each of the stems being hollow and cylindrical, and extending through a stuffing box, 23, mounted on the top of the shell, and preferably constructed with a water chamber, 24, for keeping the gland sufficiently cool. The lower end of the upper section has flanges 25, on opposite sides, adapting it to be coupled to the partly closed upper end of a flat middle section 2', which is tubular, excepting its lower end, and this end is trough-shaped in common with the lowermost section 3', which is detachably bolted to the trough-shaped lower end of the middle section 2'.

A pair of manholes, 26 and 27 (Fig. 22), in the middle section 2' of the outer shell, afford access to the bolts connecting the middle and lowermost sections 2' and 3' of the electrode stems, and facilitate disconnecting the lowermost sections 3' when the latter need to be renewed.

The electrodes proper, *h* and *i*, are of carbon, made in sections of different lengths, but all of one and the same size, and all rectangular in cross section (compare Figs. 22 and 25). Such carbon sections project at right angles from the lower ends of the stems *f* and *g*, and may be clamped within the trough-shaped stem sections 3'. A sufficient number of the longer carbon sections are united at bottom to form the main body of each electrode, and above these the shorter sections are arranged in steps, as shown in Fig. 22. The electrodes *h* and *i* project inwardly, as shown in Figs. 22 and 25, and are supported beneath by the bolster-forming lower ends of the embrasures 7 and 8, through which the respective electrodes extend toward each other, into the working chamber *a*, as shown in Fig. 22.

The tubular or hollow-stem sections 1' and 2' provide for feeding the material downwards upon the electrodes. The upper end of each stem is provided with a conical plug, 29, and with a gallows or yoke, 30, between which and the top of the plug 29 a wooden wedge, 31, is driven to render the closure air-tight.

In charging the furnace, the lower part of the working chamber *a* is filled with broken sulphur to the plane of the electrodes *h*, and a sufficient quantity of charcoal is superimposed. The lower part of the furnace is then tightly

closed and sealed, and the working chamber *a* is thereafter filled with charcoal to any desired extent by way of the charcoal hopper *a'* by depressing the bell 15 by means of the lever 17. The hopper *a'* is then automatically closed at bottom by the re-elevation of the bell 15. Crushed sulphur is fed into the annular feed space *b* surrounding the working chamber wall from time to time as required by way of the hoppers *b'*, which are filled with the sulphur, and may serve to measure the quantity introduced, and are emptied into the feed space *b* by partly withdrawing their plugs 11 and replacing them immediately to prevent the entrance of air and the escape of fumes. The disulphide vapour, as it is formed, passes off through the pipe *c* into a suitable condenser.

An upper manhole, 32, extending outward from the working chamber *a* through the shell sections 1 and 2, as shown in Figs. 22, 23, and 25, facilitates access to the interior of the furnace when it is cold for adjusting or renewing the electrodes *h* and *i*, and for arranging the charge at the beginning of an operation; and a subjacent manhole, 33 (Fig. 23), facilitates removing the ash from time to time as may be necessary. The electrode stems *f* and *g*, and their stuffing boxes 23, are insulated with mica and asbestos paper.

This furnace is designed to be 8 or 10 feet in diameter and 18 or 20 feet high, and will produce 5000 lbs. of carbon disulphide in 24 hours. Two electrodes only are employed.

Purification of Carbon Disulphide.—The crude product, which contains considerable quantities of sulphur, may be purified by distillation. The distilling vessel is made of sheet zinc, and is fitted in a water-bath. The vapours of carbon disulphide are passed through a wide tube into a worm surrounded by cold water, and ending in a lap at the bottom; the liquid as it condenses is allowed to trickle into a vessel placed to receive it.

Deiss employed large boilers with flat bottoms, which were 10 feet in length, 6½ feet in diameter, and 3½ feet high. They had domed covers, externally coated by badly conducting material, so as to reduce to a minimum the amount of carbon disulphide returned to the boiler by condensation. The boiler was capable of receiving 5 tons of crude disulphide at a single charge, and had six delivery tubes which terminated in six vertically placed condensers. At the bottom of the boiler, there were two serpentine pipes, through one of which steam was passed until the crude carbon disulphide boils. For the purpose of distilling off the last portions steam was passed through the second serpentine pipe direct into the boiler, by which means carbon disulphide vapour and steam pass over together into the condensers, when the former accumulated in a layer below the surface of the water. The distillation of 5 tons lasted 3 or 4 days, and the products of the distillation at different stages were separately collected, and served for different purposes. In the first portions, foul-smelling constituents predominate, such as sulphuretted hydrogen; the intermediate portions are the purest, while the last portions are contaminated with sulphur. Much of the sulphuretted hydrogen was removed by placing a small quantity of caustic soda in the boiler.

Bonière purified the crude material by running it into a *still* containing a strong solution of caustic soda and heated externally by steam; the vapour was then passed through several other vessels of a similar kind containing alkaline liquids, solutions of salts of iron, lead, or copper, from which it was distilled and condensed. Millon patented a process which consisted in mixing the disulphide with half its weight of milk of lime, and then carefully distilling.

Sidot first *distils* the crude product, and then agitates it with mercury till the shining surface of the metal is no longer blackened by it. Carbon disulphide, when pure, is not affected by contact with mercury for any length of time. Or it may be shaken with 0·5 p.c. of mercuric chloride, which removes a fœtid compound of sulphur. The clear liquid is then decanted, 0·02 of its weight of an inodorous fat is added, and the mixture *distilled* in a water-bath at a low temperature (Cloez).

Another method of purification is to add to 100 parts of commercial product from 2 to 3 parts of dried copper sulphate, and to shake the mixture. The copper salt blackens and settles down, with removal of the smell of sulphuretted hydrogen. Absolute purity is obtained by again rectifying over dry copper sulphate. The latter can be rendered fit for further use by ignition, treating with sulphuric acid, and again igniting. The sulphide may be retained in a state of purity by allowing it to stand constantly over dry copper sulphate (J. Soc. Chem. Ind. 2, 246).

Singer has employed the following simple method with very satisfactory results:—

A cylindrical vessel, about 30 inches in diameter and 6 feet high, is provided with a perforated coil of lead pipe at the bottom. Into this vessel the impure carbon disulphide is run to about one-third its height. Lime-water is then pumped into it by means of a force-pump through the perforated coil. The lime-water, being specifically lighter than the carbon disulphide, rises to the surface, and, while traversing the body of the disulphide in a finely divided spray, the lime combines with the sulphuretted hydrogen, &c. This washing is continued until the lime-water, which leaves this vessel through an overflow pipe near to the top, is perfectly clear. The carbon disulphide is now run into a still, about 1 p.c. its weight of a cheap colourless oil added, and covered with a layer of about 1 inch of water, to which some sugar of lead may be added. The carbon disulphide is now distilled in a water-bath and condensed in the usual way.

Carbon disulphide comes into the market in sheet-iron drums, the plates forming the top and bottom being bent inwards for their better protection from blows in moving about, and in the upper end there is an opening which can be closed by a screw stopper. Great care should be taken in the storing of carbon disulphide on account of its extreme volatility, the explosive nature of a mixture of the vapour with air, and the fact that its products of combustion are three irrespirable gases, viz. carbon dioxide, sulphurous oxide, and nitrogen. The store room ought to be isolated from other buildings, and should be well ventilated. The vessels in which the substance is kept ought to be tolerably large and placed where they are not likely to

receive a blow or get thrown over. When required for use, the carbon disulphide can be drawn off by means of a siphon.

Properties.—Carbon disulphide is a colourless and extremely volatile liquid; the commercial product has a repugnant and fœtid smell, but when purified it has a sweetish ethereal odour, and an acrid pungent taste. It is highly refractive, its power in this respect being 1·645; its sp.gr. is 1·29215, 0°/4° (Thorpe). Water dissolves about $\frac{1}{1000}$ of its volume of the disulphide, and yields it up again unchanged on distilling; the solution in water possesses the odour of the disulphide, and has a slight burning taste. The aqueous solution acts as an antiseptic. Carbon disulphide dissolves sulphur, phosphorus, iodine, bromine, chlorine, camphor, caoutchouc, oils, and fats, and may be mixed in almost any proportions with alcohol, ether, benzene, and the fixed and volatile oils. Sulphur and phosphorus may be obtained in crystals by the spontaneous evaporation of their solutions in carbon disulphide. When a rapid stream of air is passed through it, the vapour, as it rises, is condensed to cauliflower-like masses, which make their appearance on the surface of the liquid (Wartha, Ber. 3, 80). When the whole of the liquid has disappeared, the resulting solid has a constant temperature of −12°, so long as it remains unvolatilised. According to Wroblewski and Olzewski, it solidifies at −116°, and remains solid for a considerable time, emitting a peculiar aromatic odour.

Carbon disulphide boils at 46·0° (Thorpe), and the vapour ignites in air at 149°. When mixed with three times its volume of oxygen, or an amount of air containing that volume of oxygen, it is very explosive. The flame of burning carbon disulphide is blue, and gives rise to sulphurous and carbonic acid gases: $CS+3O_2=CO_2+2SO_2$. When carbon disulphide is burnt in a lamp on the principle of the Bunsen burner, and special precautions taken to prevent explosions, it produces a flame with an actinic power superior to that of magnesium (Compt. rend. 79, 1078).

A mixture of the vapour of carbon disulphide with nitric oxide burns with a blue flame, which is very rich in rays of high refrangibility, and on this account has been employed in photography.

Carbon disulphide is highly poisonous, inhalation of the vapour producing giddiness, vomiting, congestion, and finally coma. Even in small quantity only, it produces in time very serious effects on the nervous system. In the workmen employed in its manufacture, it causes weakness, depression, and loss of memory. Solution of ferrous carbonate in carbonic acid water has been found in some cases effectual as a remedy. Carbon disulphide vapour, when passed through a tube heated to bright redness, is partly resolved into its elements, carbon depositing and sulphur passing off with the undecomposed compound.

The following table represents its vapour tension at varying temperatures (Seyferth):—

45·5°	1 atmosphere
57·7	1½ „
66·9	2 atmospheres
74·3	2½ „
80·6	3 „
86·1°	3½ atmospheres
90·9	4 „
95·5	4½ „
99·0	5 „

(For table of vapour pressures between 0° and 50°, *v.* Ramsay and Young, Chem. Soc. Trans. 47, 653; also Herwig, Pogg. Ann. 137, 69; 141, 83; 147, 161.)

The vapour of carbon disulphide, when passed over metallic oxides at a red heat, yields sulphur dioxide and carbon, together with metallic sulphides, which are generally found crystallised and resemble those found in nature. Carbon disulphide is one of the most powerful sulphurising agents known, and by means of it many sulphides may be produced which are not otherwise obtainable (Frémy). It converts oxides into sulphides when heated with them in sealed tubes. The vapour is strongly attacked by nitric acid, yielding sulphuric acid and nitrous vapours.

A mixture of the vapour of carbon disulphide and sulphuretted hydrogen, when passed over red-hot copper, yields copper sulphide and marsh gas: $CS_2+2SH_2+4Cu=4CuS+CH_4$.

The vapour of carbon disulphide when passed over wood undergoing destructive distillation alters the character of the carbonaceous residue, producing a material having high conducting powers for heat and electricity, and extremely sonorous when struck.

Carbon disulphide is a powerful disinfectant. Meat and other putrescible bodies have been kept in an atmosphere containing its vapour for months without change.

Heated potassium burns in the vapour of carbon disulphide with formation of potassium sulphide and liberation of carbon.

When brought in contact with a solution of an alkaline hydroxide, carbon disulphide is decomposed, a carbonate and a sulphocarbonate being formed:

$$6KHO+3CS_2=2K_2CS_3+3H_2O+K_2CO_3.$$

When the vapour of carbon disulphide is passed over heated calcium hydroxide, it is decomposed, carbon dioxide and sulphuretted hydrogen being evolved.

This reaction has been utilised in the removal of carbon disulphide from coal gas.

Chlorine has but little action on carbon disulphide at the ordinary temperatures, but in the presence of iodine, the chlorides of antimony and molybdenum, &c., chlorine replaces the sulphur with conversion of the carbon disulphide into carbon tetrachloride, and, if the action is interrupted before it is complete, intermediate compounds or sulphochlorides are formed (J. Soc. Chem. Ind. 6, 728).

Carbon disulphide combines with triethylphosphine $P(C_2H_5)_3$ to form a solid compound, crystallising in red crystals of the composition $P(C_2H_5)_3CS_2$.

Owing to its volatility it may be made to produce great cold by its own evaporation, and if this takes place very quickly under the air-pump, a temperature of −60° may be obtained.

An aqueous or alcoholic solution of caustic potash, boiled with carbon disulphide, yields with lead salts a black precipitate of lead sulphide. This is a delicate test for the substance.

Carbon disulphide may be detected in coal

gas by passing the gas when completely freed from sulphuretted hydrogen over red-hot copper foil, when the copper acquires an iridescent lustre, and its nitric acid solution diluted with water yields after some time a precipitate with barium chloride (A. Vogel, Zeitsch. anal. Chem. [2] 6, 253).

Carbon disulphide combines with metallic sulphides, forming sulphocarbonates

$$CS_2+Na_2S=Na_2CS_3.$$

Sulphocarbonic acid is a yellow oily liquid, obtained by decomposing its potassium salt with hydrochloric acid

$$K_2CS_3+2HCl=H_2CS_3+2KCl.$$

Potassium sulphocarbonate has been used for the destruction of phylloxera.

Uses.—Carbon disulphide is applied to a large number of useful purposes, the chief of which is in the preparation of vulcanised caoutchouc, and as a solvent for the latter in the manufacture of waterproof goods, by the deposition of a thin layer of the dissolved caoutchouc on the fabric; for the extraction of fat from crude wool; fatty oils from oil seeds and pressed residues; and for the purification of paraffin. It is used in the extraction of uncombined sulphur, and of bitumen from minerals. A solution of guttapercha in carbon disulphide is employed in making seamless joints and for the preparation of caoutchouc cement, various colours, ammonium, thiocyanate, &c. It is also used for filling prisms on account of its high dispersive power.

Advantage is taken of its poisonous properties to expel weevils and other insects from stored grain without injuring the cereal. For this purpose, a small quantity of the carbon disulphide is sprinkled over the grain; both the larvæ and eggs are killed without injury to the grain (Doyère). It is also employed to destroy chicken lice and fleas, moths in furs, and in America to kill burrowing animals, such as gophers, ground squirrels, woodchucks, prairie dogs, rats, mice, moles, &c., and as a plant insecticide. It is used in Brazil to expel the Sauba ant from the foundations of houses. It may also be used in the analyses of oil seeds as a solvent for the purpose of ascertaining the proportion of oil which the ground seeds contain.

As carbon disulphide dissolves iodine in large quantity, but does not appreciably dissolve in water, it is employed for determining the amount of moisture in commercial iodine.

It may be used for dissolving quinine and other alkaloids; for extracting the aromatic principles from seeds and spices; and for the extraction of the scent of flowers. For these purposes, however, the purest quality of the disulphide can alone be employed.

A solution of phosphorus in carbon disulphide has been employed in the electrotyping of very delicate objects, such as grasses, flowers, feathers, &c. These are dipped into the solution, when, by exposure to the air, the carbon disulphide evaporates and leaves a thin film of phosphorus on the surfaces; they are then dipped into a solution of silver nitrate, by which silver is precipitated in a thin film, upon which, by the electrotype process, any thickness of silver, gold, copper, &c., can be deposited. If a few drops of carbon disulphide are put into a solution of silver cyanide, from which the metal is being electro-deposited, the silver is deposited bright, whereas without the disulphide it would be dull.

Deiss, who first employed carbon disulphide in the extraction of fatty oils from seeds, oilcakes, and other pressed residues, used the following arrangement:—

Carbon disulphide was introduced into a large cemented brickwork reservoir, with a manhole, which is generally kept closed, 22 feet long, 6 feet in diameter, and nearly 6 feet deep, and lined with lead up to the point to which it was filled with the disulphide and water, the latter being added as a thin layer to prevent the too rapid evaporation of the carbon disulphide. Immediately above this reservoir is a worm condenser, whose tail pipe dips into the liquid in the reservoir below; on one side of the condenser there is an extractor having a capacity of 4400 gallons, and capable of receiving a charge of 12 tons of oilcake. This extractor is supplied by means of a pump with carbon disulphide from the reservoir below through a pipe leading up from the reservoir to the extractor. The latter apparatus has two perforated shelves, one nearly at the top and the other nearly at the bottom, between which the substance to be operated upon is placed. In the space between the lower perforated shelf and the bottom of the extractor is a coil of pipe through which steam can be passed. Just above the upper perforated shelf there are nine pipes on the same level for the purpose of carrying the vapours produced in the operation to the condenser. There are also pipes just above this shelf which are in direct communication with a still on the opposite side of the condenser, to which disulphide saturated with oil is carried, the saturated disulphide rising to the surface in the operation owing to the difference in the sp.gr. of the carbon disulphide (1·29) and oil (about 0·900). The still in which this liquid is distilled is about 11 feet long, 5 feet wide, and 15 inches deep, holding when half filled about 400 gallons. The liquid is heated by steam supplied through two pipes coiled several times round the bottom of the still, and the vapour of the volatilised carbon disulphide is led through nine pipes into the condenser, and thence into the reservoir below the condenser, and is ready to be used again in the extractor for macerating a fresh quantity of material.

The time taken to fill the extractor with carbon disulphide is 8 hours, the maceration of the material 4 hours, the emptying of the contents of the extractor into the reservoir at the close of the operation 2 hours, and the steaming of the oil in the still in order to free it from carbon disulphide from 8 to 12 hours. Working with an apparatus such as described, about 2½ tons of oil can be obtained in 30 hours from 25 tons of oilcake.

Extraction of fat from wool.—Morson and Jerome employ for this purpose a large cylindrical vessel with a close-fitting cover and double walls, between which hot water circulates. The wool is placed on a perforated shelf near the bottom of the cylinder, whilst a perforated plate, a kind of piston, could be pressed upon the wool by an arrangement of screws. Carbon disulphide is pumped from a reservoir into the

extractor, and as the liquid becomes saturated with fat it is led through a pipe into a still, heated by a coil of steam pipe at the bottom, the vapour being passed to a worm condenser and the liquid disulphide passed into the reservoir which is immediately beneath. By a second arrangement of steam pipes, steam can be passed directly into the still so as to remove the last portions of disulphide. A current of air, heated to 70°, is then forced through the wool by means of an air-pump. As all the parts of the apparatus are in direct communication with each other, it is necessary to supply the diminished pressure in the reservoir. When air is pumped out of it and sent through a tube several times bent and the last portion fitted with a hot-water jacket, the equilibrium of pressure should be maintained, and this is done by a supply of air from a gas-holder in connection with the apparatus. The last portions of carbon disulphide are thus swept out of the extractor and are carried through a pipe into a second worm condenser, and thence to the reservoir. At convenient points between the macerating vessel and the still, as well as at the ends of the condensing worms, there are windows in the pipes, which serve to form an idea of the state of the operation, and close to each of these windows is a cock from which a little of the liquid can be drawn and evaporated, in order to see if a residue of fat remains.

The macerating vessel or extractor is charged with about 10 tons of wool, which is then reduced to about half its bulk by screwing down the perforated plate. The carbon disulphide is pumped into the extractor, and, after filtering through the wool, ascends through the perforations and passes into a pipe leading to the condenser. This is continued until the liquid comes over colourless, and leaves no residue on evaporation. When the extracting process is finished, the cock admitting carbon disulphide into the extractor is closed, and a partial vacuum is formed by drawing air out of the extractor by the air-pump, the greater part of the disulphide adhering to the wool being carried with it at the first few strokes. The water-jacket is then heated by water at 70°, and the cocks are so arranged as to allow the heated air to pass through the wool, and thence into the open air. By this method a considerable quantity of fatty substance is obtained from sheep's wool which was formerly lost.

The following materials are treated with carbon disulphide in order to obtain fatty matters from them :—

1. The dark-coloured residues of stearin manufactories, which are products of the treatment with sulphuric acid. They yield from 18 to 20 p.c. of fatty acid, which was formerly almost entirely lost. The residues are mixed with sawdust to facilitate the filtration of the dissolved portion.

2. The dark-brown cart-greese from the axles of carts, carriages, &c. This is first treated with sulphuric acid, washed, and dried.

3. Tow and rags used in cleaning machinery. This treatment of rags, &c., has a threefold advantage; recovery of fat or fatty acids, purification of the rags so that they can be used again, and the prevention of spontaneous combustion, which these materials are liable to on exposure to air.

4. The refuse of the preparation of beeswax, which on treatment with carbon disulphide yields a yellow wax useful for many purposes.

5. Sawdust that has been used for filtering oils after purification with sulphuric acid.

6. The sediment produced by the treatment of various oils with sulphuric acid contains about 50 p.c. of oil, which may be extracted by carbon disulphide after washing with boiling water, drying, and mixing it with sawdust.

7. Bones from slaughter-houses and kitchens to be used in the preparation of bone-black yield to carbon disulphide from 10 to 12 p.c. of fat.

8. The expressed residues of oil seeds, such as rape, sesamé, flax, &c., when they cannot be properly employed as fodder. In all cases it is necessary to break up the oilcake into small pieces before treating it with carbon disulphide, so as to ensure thorough penetration of this substance. The residue left after extracting the fat is hardly suitable for fodder, but is valuable as a manure.

9. The 'cracklings' or greaves obtained by the melting of tallow.

10. The pressed cacao beans from which no further cacao butter can be obtained by pressing.

11. The pressed residues obtained in the preparation of olive oil.

Extraction of bitumen, &c., from minerals.—Carbon disulphide can be employed in the extraction of bitumen from mineral bodies which contain so small a percentage as not to pay when obtained by the ordinary process of distillation. The apparatus used consists of a close reservoir for the carbon disulphide, over which is a cooling apparatus which serves as condenser. Below the reservoir are two filters provided near the bottom with perforated shelves. Minerals are introduced into the filters upon the shelf through doors near the bottom, which are then closed and made air-tight. Carbon disulphide is now admitted through a pipe at the bottom of each filter, and as the liquid rises it percolates through the minerals, dissolving out the bitumen, and when full flows out at the top through a pipe leading to a still, where the saturated liquid is distilled, the vapour of carbon disulphide ascending into the condenser, and the liquid carbon disulphide as it condenses trickles into the reservoir beneath. The bituminous matters, which remain in the still, are drawn off by a cock at the bottom, and the disulphide which remains absorbed by the minerals in the filters is expelled by a current of steam. This apparatus is practically continuous, very little loss of the disulphide taking place at each operation, and as much as 12 p.c. of bitumen can be obtained, whereas only 7 or 8 p.c. could be had by distillation.

Extraction of spices, &c.—Bonière has devised an apparatus for extracting the aromatic principles of various spices and other substances used for seasoning food, by means of carbon disulphide. It is on the same principle as the apparatus already described, and consists of a series of wire-gauze sieves arranged one over the other in an air-tight case. The carbon disulphide is made to pass through the sieves, which contain the substance to be operated upon, *e.g.* pepper, thus dissolving out the active principles, and as it reaches the top it flows through a pipe

into a boiler. The boiler contains either salt, sugar, lactose, dextrin, saltpetre, or other material. The liquid is distilled in the boiler, by admitting steam into a kind of jacket, when the disulphide distils over and is condensed in a worm condenser, while the salt or sugar remains behind, retaining all the aromatic or active principles of the spice.

Bergot has constructed an apparatus for rapidly determining the quantity of oil in seeds, &c., by means of carbon disulphide. It consists of a glass vessel in the neck of which a cylindrical glass vessel is accurately fitted, and at the side in a tubulure is inserted a small air-pump. 50 grams of the finely ground seed to be examined are placed in the cylindrical glass vessel, and are covered with a diaphragm upon which 50 more grams are placed and covered with a second diaphragm. Carbon disulphide is now poured on until the seed is fully moistened, and after a few minutes a partial vacuum is made in the apparatus by means of the air-pump, when the pressure of the air drives out the disulphide and oil in solution into the vessel beneath. This is repeated until the carbon disulphide comes off colourless and leaves no oily stain on contact with filter paper. About 400 or 500 grams of carbon disulphide are sufficient to exhaust the above amount of seed.

The oily solution thus obtained is heated over a water-bath, and as soon as the disulphide is expelled, the residue is allowed to cool and is weighed.

H. L. Greville has extracted with advantage the carbon disulphide absorbed in the purifiers of the gasworks. The lime used for this purpose, after being discharged from the purifiers, is introduced into a boiler capable of receiving a charge of several hundredweights, fitted with a perforated false bottom, pressure gauge, and an arrangement for admitting steam. The yield of carbon disulphide from 100 tons of spent lime is about 1½ tons. In addition to the value of the crude product thus obtained, the lime remaining is, with a small addition of fresh lime, fit for further use in the purification of coal gas. As is well known, oxide of iron, after continued use in the absorption of sulphuretted hydrogen from coal gas, contains about 50 p.c. of free sulphur. The crude carbon disulphide, obtained as described, can be used for the extraction of this sulphur, and the oxide which remains is revivified, and is again fit for purifying purposes. The sulphur is recovered by distillation, and the carbon disulphide can be used over again (J. Soc. Chem. Ind. 2, 488).

The principal seats of manufacture of carbon disulphide in England are London, Manchester, certain towns in Yorkshire, and Ironbridge; in France, Paris, Bordeaux, and Marseilles. Germany, Austria, and Sicily have several manufactories.

Carbon monosulphide (xCS). A reddish-brown powder obtained by exposing carbon disulphide to sunlight. Insoluble in water, alcohol, turpentine, and benzene (Sidot, Compt. rend. 69, 1303; 74, 180; 81, 32).

It is also formed when thiocarbonyl chloride reacts at ordinary temperature with nickel carbonyl: $xCSCl_2+xNi(CO)_4=xNiCl_2+4xCO+(CS)_x$. The reaction also takes place at −20°, although more slowly. The nickel chloride produced is extracted with water, and the brown residue is dried by heating at 100°, then at 150°–200° under reduced pressure.

Carbon monosulphide has sp.gr. 1·6, but after compression into a solid block the sp.gr. is 1·83. It is a non-conductor of electricity. In concentrated sulphuric acid it forms a purplish-brown solution, the colour of which is destroyed on boiling, when carbon dioxide and sulphur dioxide are evolved. When poured into water the purplish-brown solution yields the unchanged monosulphide. It also forms brown solutions in aqueous or alcoholic ammonia, in ammonium sulphide, in potassium-hydroxide sulphide and hydrosulphide. With nitric acid it gives a red solution. When heated in a vacuum at 360° or below, no change takes place, only a small quantity of hydrogen sulphide is evolved, but at a dull red heat it decomposes thus:

$$2(CS)_x = xC+xCS_2.$$

When carbon disulphide vapour at low pressure is subjected to the action of the silent electric discharge, sulphur is deposited, and probably gaseous carbon monosulphide is evolved. The gas can be collected in a tube cooled with liquid air, when it condenses together with carbon disulphide. If the temperature of the condensing tube is allowed to rise, the monosulphide polymerises with explosive violence to the brown solid carbon monosulphide $(CS)_x$. In presence of excess of carbon disulphide, the gaseous monosulphide is fairly stable under certain conditions even at high temperatures, but it is completely decomposed when passed through 10 c.m. of a red-hot tube packed with asbestos. (Dewar and Jones, Proc. Roy. Soc. 1910, 83, A, 408, 526. *See* also Dunn, Chem. Soc. Proc. 1910, 116; Dewar and Jones, *ibid.* Trans. 1910, 1226.)

Carbon oxysulphide or Carboxyl sulphide or Carbonyl sulphide COS. Discovered by Than, in 1867; occurs in certain hepatic waters or mineral springs. Prepared (1) by passing a mixture of carbonic oxide and vapour of sulphur through a hot tube: $CO+S=COS$.—(2) By the action of sulphuric acid upon potassium or ammonium thiocyanate:

$$CNKS+2SO_4H_2+OH_2 = COS+SO_4HK+SO_4H(NH_4).$$

The gas is purified by passing it successively through strong caustic alkali, concentrated sulphuric acid, and finally through a mixture of triethylphosphine (1 part), pyridene (9 parts), and nitrobenzene (10 parts). It is then cooled to 10°–20°, and the last traces of impurities are removed by liquefying it, when the impurities remain uncondensed (Hempel, Zeitsch. angew. Chem. 1901, 14, 865).—(3) By heating together sulphur trioxide and carbon disulphide: $CS_2+3SO_3=COS+4SO_2$ (Armstrong).—(4) By heating urea with carbon disulphide in a sealed tube to 110°: $COH_4N_2+CS_2=COS+CNS{\cdot}NH_4$. The oxysulphide is given off together with hydrogen sulphide on opening the tube, and the latter is absorbed by passing through lead acetate (Ladenburg). It is also formed in the combustion of carbon disulphide with oxygen (Dixon and Russell, Chem. Soc. Trans. 1899, 610), and by the passage of the dark electric discharge through a mixture of carbon disulphide

and carbon monoxide (Losanitsch and Jovitschitsch, Ber. 1897, 30, 135).

Properties.—Is a colourless gas smelling like hydrogen sulphide, but with a slight aromatic odour. It acts strongly on the nervous system, a rapid overpowering action following the inhalation of small quantities. It is readily inflammable, and forms with oxygen an explosive mixture (Russell, Chem. Soc. Trans. 1900, 356). The gas is soluble in water, 1 c.c. dissolving 0·8 c.c. of the gas at 13·5° and 756 mm. pressure. The solution acquires its characteristic taste and smell, but gradually decomposes, forming hydrogen sulphide and carbon dioxide. A platinum wire heated to whiteness in the gas decomposes it into sulphur and carbonic oxide, the latter occupying the original volume of the gas. It has a specific gravity of 2·1046, and may be easily poured from one vessel to another. When burnt in air, it produces carbon dioxide and sulphur dioxide. With caustic alkalis, it yields a mixture of carbonate and sulphide

$$COS+4KHO=CO_3K_2+K_2S+2H_2O.$$

Carbon oxysulphide reacts with solutions of metallic salts, forming the metallic sulphide and carbon dioxide, and is readily oxidised to carbon dioxide and sulphuric acid by bromine water or acid permanganate.

It is slowly decomposed by acid cuprous chloride; thus:

$$COS+2CuCl+H_2O=CO_2+2HCl+Cu_2S$$

(Berthelot, Ann. Chim. Phys. 1898, [7] 14, 205).

With magnesium organic compounds, it can be employed in the synthesis of thio-acids and of *s*-trisubstituted carbinols (Weigert, Ber. 1903, 36, 1007).

Its critical temperature is 105°, and its critical pressure is 60 atmospheres. It is liquefied at a pressure of 12·5 atmospheres and temperature 0° to a colourless, mobile, and highly refractive liquid, boiling at −47·5° at 760 *mm.*, which dissolves sulphur and mixes with alcohol and ether, but not with water. If the pressure is suddenly released, solid flakes are deposited, and persist for some time (Ilosvay, Bull. Soc. chim. [2] 37, 294).

CARBON SUBOXIDE (*Carbon carbonyl*; *Carbonyl ketene*; *Malonic anhydride*) C_3O_2. Discovered in 1906 by Diels and Wolf. Prepared by distilling ethyl malonate under reduced pressure into a vessel containing a large excess of phosphorus pentoxide and some glass wool, the vessel being kept at a temperature of 300°. The resulting products are passed through a dry tube, and then into a vessel immersed in liquid air to condense the ethylene and carbon suboxide. The ethylene volatilises from the mixture at the ordinary temperature, leaving a small quantity of colourless liquid. This is volatilised and collected in a tube kept at between 60° and 70° (Diels and Wolf, Ber. 1906, 689). Diels and Meyerheim (*ibid.* 1907, 355) showed that carbon suboxide may be obtained by similar methods from methyl, benzyl, and phenyl malonates and also from ethyl methanetricarboxylate; and that by heating malonic acid at 140°–150° there is formed acetic acid, carbon dioxide, and about 10–12 p.c. of carbon suboxide. Staüdinger and Bereza obtained carbon suboxide by treating malonyl chloride with silver, lead, or zinc oxides; the yield is only 10 p.c. (Ber. 1908, 4461). By treating an ethereal solution of dibrommalonyl chloride with zinc shavings, a method similar to that for preparing the ketenes, Staüdinger and Klever obtained a 50–80 p.c. yield of carbon suboxide (Ber. 1908, 906).

The pure oxide is a colourless, very mobile, refractive liquid with a pungent smell resembling acetaldehyde and mustard oil. It is poisonous. It boils at 7° under 761 mm., and its vapour density corresponds to the formula C_3O_2; m.p. −107°; density of liquid 1·11. On passing the vapour through a constricted tube, a metallic mirror resembling arsenic is obtained. At low temperatures, carbon suboxide is quite stable, but between 0° and 15° a trace of impurity rapidly polymerises it to a red solid. This polymeride is very hygroscopic, and on addition of water, heat is developed, carbon dioxide evolved, and an eosin-red solution formed: by heating the red compound carbon dioxide, carbon monoxide and carbon suboxide are formed, and at higher temperatures, carbon monoxide and dioxide are produced, the residue being a mixture containing more carbon than is required for carbon suboxide. By keeping carbon suboxide for 2 days in a sealed tube at 15°, it completely changes into the polymeride, forming a dark-red solid mass, soluble in water to a dark-red solution; this change is instantaneous at 100°. Carbon suboxide burns with a bright-blue but smoky flame, forming carbon dioxide. Carbon suboxide does not combine with aldehydes, Schiff's bases or hydrogen cyanide (Diels and Lalin, Ber. 1908, 3426), but in liquid sulphur dioxide at −40° to −50° forms a white crystalline compound with formic acid, and a colourless syrup with acetic acid; the constitution of these compounds is doubtful.

Two formulæ have been proposed for carbon suboxide; Diels and Wolf represent it as the anhydride of malonic acid $O:C:C:C:O$; Michael (Ber. 1906, 1915; 1908, 425), as the lactone of β-hydroxypropiolic acid $C\equiv C(CO)>O$. The first formula seems to be correct, for the following reasons (*v.* Diels and Blumberg, Ber. 1908, 82, 1233):—

(1) B.p. 7°. Propiolic acid boils at 144°, and if β-hydroxypropiolic acid had a boiling-point, it would boil higher still, and its lactone would certainly not boil at so low a temperature as 7°.

(2) The values for the molecular refraction and molecular dispersion are high: $M_D=16·6$; $\gamma-\alpha=0·736, 0·739, 0·862$ (three determinations).

(3) Similarity of carbon suboxide to the metallic carbonyls.

(4) Similarity to the isocyanates and ketenes.

(5) Addition of four atoms of bromine to form dibrommalonyl bromide and the regeneration of carbon suboxide from this compound.

(6) The following chemical reactions:—

$O:C:C:C:O+2H_2O=HOOC\cdot CH_2\cdot COOH$ (malonic acid).

$O:C:C:C:O+2HCl=ClOC\cdot CH_2\cdot COCl$ (malonyl chloride).

$O:C:C:C:O+2NH_3=H_2N\cdot OC\cdot CH_2\cdot CONH_2$ (malonamide).

$O:C:C:C:O+2C_6H_5NH_2=C_6H_5\cdot HN\cdot OC\cdot CH_2\cdot CONH\cdot C_6H_5$ (malonanilide).

(7) The improbability of the existence of a-β-lactone containing two carbon atoms triply linked together (*v.* KETONES).

CARBONADO *v.* DIAMOND.

CARBONITE, or natural coke. A coke-like

material formed by the baking action of intrusive igneous rock-masses on seams of bituminous coal. Found in Ayrshire and in Chesterfield co., Virginia. L. J. S.

CARBONITE. An explosive consisting of nitroglycerine, 25–27 parts; barium nitrate and potassium nitrate, 30–36 parts; wood meal, 40–43 parts; sodium carbonate, 0·5 parts (*v.* EXPLOSIVES).

CARBONYLS. Metallic compounds of carbon monoxide. The existence of this class of compounds was first made known in 1890, when Mond, Langer, and Quincke discovered that carbon monoxide, passed over heated, finely divided nickel, yielded a colourless volatile liquid.

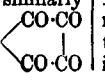
Iron, cobalt, molybdenum, and ruthenium have since been found to yield carbonyls by similar treatment.

The production of the carbonyl is facilitated by conducting the operation under pressure and, in most cases, at a fairly high temperature.

For the production of the iron and nickel compounds, the carbon monoxide is simply passed over the heated metal, but for the other compounds a special apparatus is used. This consists of a nickel-steel tube, in the form of a test-tube, capable of withstanding a pressure of 500 atmospheres and a temperature of 450°. It is copper lined to prevent the action of carbon monoxide upon the iron. The carbon monoxide under pressure is led in through a pressure valve and down a copper tube reaching almost to the bottom of the nickel-steel tube, where it comes in contact with the metal to be experimented upon, contained in a glass tube loosely fitted to the top of the apparatus. The excess of the carbon monoxide, and other vapours, escape through a pressure valve and pass through a tube immersed in a freezing mixture, in which any compound that is formed is collected (Chem. Soc. Trans. 1910, 97, 798).

The carbonyls have very similar chemical properties. Upon heating, in some cases an intermediate compound is formed, but they all decompose ultimately, yielding the metal, which is deposited. as a bright mirror, and carbon monoxide. Dilute acids are practically without action upon them, but strong acids decompose them readily, giving the corresponding salt, with the evolution of carbon monoxide and hydrogen. The halogens also decompose them. All are decomposed by moist air, giving precipitates of the metallic hydroxides and, in some cases, what is probably a hydrated basic carbonate. They are more or less soluble in the common organic solvents, but all are insoluble in water.

In physical properties, they vary considerably; thus, in volatility, they range from the non-volatile $Fe_2(CO)_9$ of sp.gr. 2·08 to the very volatile $Ni(CO)_4$ of sp.gr. 1·32. They are highly coloured, except in the cases of molybdenum and nickel carbonyls, which are white and colourless respectively. Some can exist in the three states of solid, liquid, and vapour, and others in only one or two of these phases.

Owing to their diversity in composition, a general chemical formula cannot be assigned to them, but it is probable that they are similarly constituted. A ring formula, *e.g.* 

does not explain all their properties, and the compound $Fe_2(CO)_9$ cannot be brought into line with the other compounds which only contain one atom of the metal. Presumably they have a molecular rather than an atomic constitution (Mond, Hurtz and Cowap, *l.c.*). The various known carbonyls are described under the several metals.

CARBORUNDUM (*Crystalline silicon carbide*) SiC. This compound was discovered accidentally by Acheson, in 1891, and is now manufactured under his patent (Eng. Pat. 17911, 1892) by the Carborundum Co. at Niagara Falls, U.S.A., and to a smaller extent in Canada.

Preparation.—Amorphous silicon carbide is formed by heating carbon and silica together at about 1200°, as a greenish powder (Schutzenberger, Compt. rend. 114, 1089), but carborundum is only formed at a temperature of 1950° (Tucker and Lampen, J. Amer. Chem. Soc. 1906, 28, 853) (1820° according to Gillett), which is attained by means of the electric arc. Moissan thus prepared pure silicon carbide from the vapours of carbon and silicon (Compt. rend. 1893, 114, 1089).

The method of manufacture used at Niagara is as follows:—The furnaces are built of firebrick and are about 16 feet long × 5 feet high × 5 feet wide. The ends are solid, about 2 feet thick, and carry the terminals. Each terminal consists of 60 carbon rods, 30 inches long and 3 inches diameter, into the ends of which fit copper plugs which in turn fit into sockets in a square copper plate bolted to the outside of the wall, and connected with the leads. Only the end walls and the bed are permanent; the sides are built up with the charge and taken down to remove the product.

In charging, the furnace is half filled with the materials, which must not touch the electrodes; and a cylindrical core 21 inches diameter, composed of pieces of coke ½–¾ inch diameter, is built up between the electrodes. Over this the charge is built up to a height of 8 feet. The current passes through the coke and forms numerous arcs which heat the charge to a very high temperature. The charge is composed of:

Coke	34·2 parts
Sand	54·2 „
Sawdust	9·9 „
Salt	1·7 „

The salt is added as a flux; the sawdust to increase the porosity of the charge and allow the escape of the carbon monoxide formed in the reaction:

$$SiO_2+2C=Si+2CO$$
$$Si+C=SiC.$$

During the run, about 6 tons of this gas are given off; it is allowed to burn at the top of the furnace.

The alternating current supplied by the Niagara Power Co. at 2200 volts is transformed down to 165 volts, and a large water rheostat is used to regulate or interrupt the current, the usual means being too dangerous with the heavy currents used. At the beginning of a run, the E.M.F. is 165 volts, but within 1½ hours the resistance decreases and the E.M.F. is reduced to 125 volts; during this period, the current increases from 1700 amperes to 6000 amperes.

The conditions then remain steady during the whole run of 36 hours.

A modification of the process consists in preheating the charge by combustion of gaseous or solid fuel (Tone and the Carborundum Co. U.S. Pat. 908357, 1908). By moving the position of the arc relatively to the charge, the process may be made continuous (*ibid.* U.S. Pat. 937119, 1909).

The charge per furnace is about 30,000 lbs., of which the core forms about 3 p.c., the energy used is about 26,400 kilowatt-hours, and the product contains about 6700 lbs. of carborundum and 5000 lbs. of amorphous silicon carbide.

The carborundum is dug out in large masses and pounded with water in a mechanical crusher, and then digested with sulphuric acid (1 : 2) for 3 days at 100°, and finally washed with water. The finer portions, which are washed away, are collected separately and known as *flours*. The residue is dried in a kiln and graded through a system of screens. *Hand-washed powders* are of various grades of fineness, according to the length of time they remain suspended in water (Kohn, J. Soc. Chem. Ind. 1897, 863).

Some analyses of these products are tabulated below :—

——	I.	II.	III.	IV.	V.
Si	70·00	69·93	62·70	69·10	65·42
C	30·00	29·90	32·26	30·20	27·93
Al_2O_3 } Fe_2O_3 }	—	—	0·93	0·46	5·09
CaO	—	—	—	0·15	0·38
MgO	—	—	0·11	—	0·21

I. is the calculated composition for SiC; II. is Moissan's pure product (Compt. rend. 1893, 114, 1089); III. is commercial carborundum; IV. is the same after purification by Mühlhäuser's method—heating in oxygen for 1 hour and treating with hot sulphuric and hydrofluoric acids (Dingl. poly. J. 1893, 289, 164); V. is amorphous silicon carbide.

Weber has patented a method of production from kaolin and coke in the electric furnace. The product is treated with water, which decomposes the aluminium carbide, leaving the carborundum (U.S. Pat. 728528, 1903).

The production of a dense, compact variety, by the action of the vapours of carbon and silicon upon silicon carbide has been patented by the Carborundum Co. (U.S. Pat. 913324) and by Bouvier (Fr. Pat. 350369, 1904). It is very hard, resists acid, and is a good insulator.

Its preparation from silicon monoxide and carbon has been described by Potter and Westinghouse (U. S. Pat. 875673, 1907).

Articles may be formed in pure carbon and afterwards converted into carborundum by heating to a very high temperature in a bed of finely powdered carborundum or of sand and carbon (Bölling, Eng. Pat. 6693, 1905; D. R. P. 195533; Fr. Pat. 353017).

Properties.—Carborundum crystallises in flattened hexagonal rhombohedra, having an adamantine lustre and a hardness of 9·5 (Mühlhäuser, Zeitsch. anal. Chem. 1893, 637). The colour of the commercial product is greenish-grey to yellow or blue; obtained pure from pure materials, the compound is colourless. Its sp.gr. is 3·23 at 15° (Fitzgerald, J. Soc. Chem. Ind. 1897, 246).

It is infusible and quite unaffected up to a temperature of 2220°, when it decomposes into silicon and graphitic carbon (Tucker and Lampen, J. Amer. Chem. Soc. 1906, 28, 853). Acids have no action upon it, but it is attacked by fused alkalis with formation of a silicate and carbon.

The determination of silicon in carborundum is made by converting it to silicate as above, and precipitating as silica; carbon is estimated by oxidising the finely powdered substance with lead chromate (Matthews, J. Soc. Chem. Ind. 1895, 755; Mühlhäuser, Zeitsch. anal. Chem. 1893, 637).

Uses.—Carborundum is used chiefly instead of emery as an abrasive. Though it is more costly, it does the same work more effectively in one-third to one-fourth the time (Mühlhäuser, *l.c.*). The powder is used in glass cutting and grinding, and for polishing.

It is made up into wheels, hones, &c., by mixing with moistened kaolin and felspar, moulding under hydraulic pressure, and firing the articles in a kiln for 7 days. Other binding materials, such as shellac, are used for special purposes, and papers, similar to emery paper, are made. The binding material may be dispensed with by moulding the carborundum with water and then heating the articles to 2500°F. in an oxidising flame (Imray, Eng. Pat. 9963, 1904; Tone, U.S. Pat. 772262).

Carborundum can be used instead of diamond for drill heads, if incorporated in a suitable metallic or ceramic matrix (Bouvier, Fr. Pat. 375338, 1907).

Silicon carbide is used instead of ferro-silicon as a source of silicon in steel making. About 0·1–0·4 p.c. is placed in the ladle and dissolves readily in the molten steel, ensuring solid castings (Kaufmann and Bouvier, Fr. Pat. 344906, 1904; Eng. Min. J. 75, 481).

The amorphous silicon carbide, formerly a waste product, is used for making highly refractory firebricks and the retorts for zinc distilling (Chesneau, Ann. Chim. anal. appl. 1908, 13, 85). A refractory cement is made from carborundum 90–60 parts, fireclay 10–40 parts, lime 0–4 parts, and water-glass solution 47°Bé. 20–50 parts, mixed, dried, and repowdered (Müller, Fr. Pat. 338914, 1903).

Neumann has shown that silicon carbide reduces silver, copper, nickel, and lead from the chlorides (Chem. Zeit. 1900, 24, 1013).

By the action of silicon carbide on metallic oxides, many metallic silicides may be obtained. This reaction may be used for the preparation of special ternary or quaternary steels at a single operation (Baradac-Muller, Soc. Mg. Cie. de France, Proc.-verb. 1908, 245).

CARBURINE. Trade name for a variety of petroleum spirit; sp.gr. 0·68. Used as an 'enricher' of coal gas.

CARDAMOM OIL *v.* OILS, ESSENTIAL.

CARDINAL-RED. Syn. *Acid magenta* (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

CARDOL. A non-volatile oil found in the

pericarp of the cashew nut, *Anacardium occidentale* (Linn.).

CARICIN. An oil found in the seeds of the papaw tree, *Carica papaya* (Linn.) (Peckolt, Pharm. J. [3] 10, 343).

CARMINAPH *v.* AZO- COLOURING MATTERS.

CARMINAPH GARNET *v.* AZO- COLOURING MATTERS.

CARMINAZARIN *v.* COCHINEAL.

CARMINE. The red colouring matter extracted from the cochineal insect. It is of somewhat variable composition, containing besides the colouring matter some organic matter from the insects and a little of the salt used to precipitate it from solution.

Preparation.—The powdered cochineal is boiled with water, the solution filtered or allowed to settle, and the colouring matter precipitated by addition of some salt, such as alum, stannous chloride, cream of tartar, Roman alum, &c. The precipitate is allowed to settle, and collected. Sometimes fish glue or white of egg is added before precipitation. Carmine is somewhat soluble in water and very freely soluble in alkaline solutions. The whole of the colouring matter is immediately precipitated by alum in the form of a lake.

In dyeing with carmine, a mordant of alum or stannous chloride is used. Kielmeyer recommends the following mixture for printing on woollen goods: 14 kilos. gum, 17·5 kilos. cochineal lake, and 2·25 kilos. fustic lake, are mixed and warmed with 15 lit. water till the gum is dissolved, then 1 kilo. of oxalic acid and 1·75 kilos. acid sodium oxalate added, and the mixture allowed to cool, after which 2·25 kilos. sodium acetate are added. After printing, the fabric must be dried for a day or two, steamed under a slight pressure, and washed in a stream of water.

Detection of carmine in cloth.—Alcohol takes no colour from the cloth, but when it is boiled in solution of aluminium sulphate the solution turns red and the colour is unchanged by the addition of acid sodium sulphate.

The absorption spectrum of carmine in alkaline solution is remarkable, showing two dark bands between the lines D and E very similar to those of blood. Murexide and madder show no such bands. When wine is coloured with carmine, the characteristic absorption bands cannot be seen unless more than 12 p.c. of the total colour is due to carmine (Gautier), but the adulteration can be detected by adding alum, when the colour changes to a rose tint.

It is said that the finest shades of carmine can only be obtained by working in direct sunlight (*v.* COCHINEAL).

CARMINIC ACID *v.* COCHINEAL.

CARMOISINE. Syn. for *Azorubin* (*v.* AZO-COLOURING MATTERS).

CARMUFELLIC ACID $C_{12}H_{20}O_{16}$. An acid crystallising in thin plates, said to be formed by the action of nitric acid on oil of cloves (Muspratt and Dawson, Phil. Mag. [4] 2, 293).

CARNALLITE. A double chloride of potassium and magnesium $KCl{\cdot}MgCl_2{,}6H_2O$, found at Stassfurt, Prussia, in a thick layer under rock-salt beds, and accompanied by the minerals *Anhydrite, Kieserite, Tachhydrite, Sylvite, Kainite*, and *Boracite*.

Analyses by Rose.

	1	2
Magnesium chloride .	31·46	30·51
Potassium chloride .	24·27	24·27
Sodium chloride . .	5·10	4·55
Calcium chloride .	2·62	3·01
Magnesium sulphate .	0·34	1·26
Oxide of iron . .	0·14	0·14
Water (by diff.) . .	36·07	36·26
	100·00	100·00

Hammerbacher found traces of cæsium, rubidium, and thallium in Stassfurt carnallite and in crystals resembling carnallite from a spring of Nauheim.

Properties.—Amorphous masses of a fatty lustre on fresh fracture, deliquescent and freely soluble, leaving a residue of iron oxide.

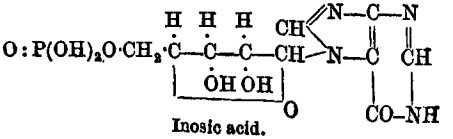
Used as a source of potassium salts and as a manure (*v.* POTASSIUM).

CARNAÜBA WAX or **CARNAHUBA WAX** *v.* WAXES.

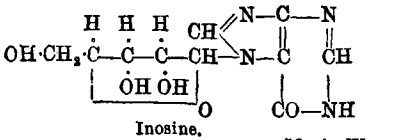
CARNAÜBIC ACID $C_{23}H_{47}COOH$ is obtained from Carnaüba wax; m.p. 72·5° (Sturcke, Annalen, 129, 168; Darmstaedter and Lifschütz, Ber. 1896, 619, 2899).

CARNINE is the name given to a base isolated from meat extract by Voit (Weidel, Annalen, 1871, 158, 353); it occurs also in beer yeast extract (Schutzenberger, Chem. Zentr. 1877, 73), in the muscle of some fresh-water fish and frog's flesh (Kruckenberg and Wagner, *ibid.* 1884, 107), and in beet juice (v. Lippmann, Ber. 1896, 29, 2645). Carnine crystallises in chalk-white druses, is sparingly soluble in cold, readily so in hot water, insoluble in alcohol or ether; it forms a crystalline *hydrochloride* and *platinichloride*, and a sparingly soluble compound with silver nitrate (Weidel, *l.c.*).

Haiser and Wentzel (Monatsh. 1908, 29, 157) have shown that *carnine* is an approximately equal molecular mixture of hypoxanthine and *inosine* $C_{10}H_{12}O_5N_4$, and the two are separated by the action of acetic anhydride which converts the inosine into the *acetate* $C_{10}H_9O_2N_4(OAc)_3$, m.p. 236° (decomp.). Inosine crystallises in silky needles, m.p. 215° (decomp.), $[\alpha]_D^{18°}-49·2°$, and 100 c.c. of aqueous solution saturated at 20° contains 1·615 grams. When inosine is hydrolysed by sulphuric acid it yields hypoxanthine and a *pentose*, originally termed *carnose* by Levene and Jacobs (Ber. 1909, 42, 2102, 2474), and afterwards identified with *a-ribose*. Inosine is closely related to *inosic acid* (*hypoxanthine phosphoriboside*) (Levene and Jacobs, *ibid.* 1910, 43, 3147; Proc. Amer. Soc. Biol. Chem. 1910, 25; Haiser and Wentzel, Monatsh. 1909, 30, 147), for by heating a dilute aqueous solution of barium inosate at 125°–130° for 6 hours, inosine and barium phosphate are formed. The relation between the two compounds is probably represented by the following formulæ:



Inosic acid.



Inosine.

M. A. W.

CARNITINE $C_7H_{15}O_3N$, a base isolated from Liebig's beef extract and present also in fresh beef; is readily soluble in water yielding an alkaline solution, the *nitrate* crystallises in needles and has $[\alpha]_D$ about $-22°$; the *platinchloride* $C_{14}H_{33}O_5N_2PtCl_6$ forms minute orange-red needles, m.p. 214°–218° (decomp.) (Gulewitsch and Krimberg, Zeitsch. physiol. Chem. 1905, 45, 326); the *hydrochloride* is hygroscopic and lævo-rotatory. The *aurichloride*

$$C_7H_{15}O_3NAuCl_4$$

forms pale yellow needles and orange needles or prisms, m.p. 150°; the *mercurichloride*

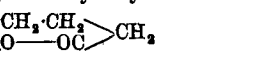
$$C_7H_{15}O_3N,HCl,6HgCl_2$$

is an oil that slowly crystallises; the *compound* $C_7H_{15}O_3N,2HgCl_2$ has m.p. 196°–197° (Krimberg, *ibid.* 1907, 50, 361). The *monoacetyl derivative* of the hydrochloride, $OAc\cdot C_7H_{15}O_2N,HCl$ forms a yellow crystalline *platinichloride*

$$(C_9H_{18}O_3N)_2PtCl_6,$$

m.p. 199° (Engeland, Ber. 1909, 42, 2457). The *ethyl ester* is identical with Kutscher's *oblitine* (Zeitsch. Nahr. Genussm. 1905, 10, 534), (Krimberg, Zeitsch. physiol. Chem. 1908, 56, 417; Ber. 1909, 42, 3878; Engeland, *l.c.*).

Carnitine is identical with Kutscher's *novaine* (Krimberg, Zeitsch. physiol. Chem. 1908, 55, 466; Engeland, Ber. 1909, 42, 2457), and is probably a hydroxy derivative of a betaïne, since on reduction with hydrogen iodide and red phosphorus at 130°, it yields a product identical with Willstätter's γ-trimethylbutyrobetaïne



(Ber. 1902, 35, 584); Krimberg (Zeitsch. physiol. Chem. 1907, 53, 514). According to Engeland (Ber. 1909, 42, 2457; 43, 2705) and Rollett (Zeitsch. physiol. Chem. 1910, 69, 60), carnitine hydrochloride is the chloride of *a*-hydroxy-γ-trimethylamino-*n*-butyric acid

$$NMe_3Cl\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H$$

M. A. W.

CARNOSINE $C_9H_{14}O_3N_4$, a base isolated from Liebig's extract of beef, is soluble in water, crystallises in microscopic needles, decomposes at 241°–245°, and has a strongly alkaline reaction. The *nitrate* $C_9H_{15}O_6N_5$ crystallises in soft needles, melts and decomposes at 211°, and has $[\alpha]_D^{20°}$ $+22·3°$; the *copper* derivative

$$C_9H_{14}O_4N_4Cu$$

is crystalline and decomposes at 220°. The *silver* derivative and acid double salt with silver nitrate closely resemble the corresponding derivatives of arginine (Gulewitsch and Amiradžibi, Ber. 1900, 33, 1902). Carnosine is probably identical with Kutscher's *ignotine* (Zeitsch. Nahr. Genussm. 1905, 10, 528; Gulewitsch, Zeitsch. physiol. Chem. 1906, 50, 204; 51, 258; 52, 527). Compare, however, Kutscher (*ibid.* 1907, 50, 445; 51, 545).

When carnosine is hydrolysed by boiling with barium hydroxide it yields histidine, the other product of hydrolysis being probably alanine

$$C_9H_{14}O_3N_4+H_2O=C_6H_9O_2N_3+C_3H_7O_2N$$

M. A. W.

CARNOTITE. A hydrated vanadate of uranium and potassium, occurring abundantly as a bright canary-yellow powder disseminated in sandstone in western Colorado. C. Friedel and E. Cumenge (Compt. rend. 1899, 128, 532), by whom it was first described and named (after A. Carnot), expressed the composition by the formula $2U_2O_3\cdot V_2O_5\cdot K_2O\cdot 3H_2O$. Detailed analyses were made by W. F. Hillebrand (Amer. J. Sci. 1900, 10, 120), and he concluded that the mineral is not simple, but a mixture. This view is, however, not borne out by T. Crook and G. S. Blake (Min. Mag. 1910, 15, 271), who find that the material, both from Colorado and from South Australia, is definitely crystallised in minute plates possessing orthorhombic symmetry and with characters analogous to those of autunite $[Ca(UO_2)_2P_2O_8,8H_2O]$. The original material was found by M. and Mme. Curie to contain radium and polonium.

The carnotite-bearing sandstones occur over an extensive tract of country on both sides of the Colorado-Utah boundary, the richest deposits being in the neighbourhood of La Sal Creek, Roc Creek, and Paradox Valley, in Montrose Co., and in San Miguel and Dolores Cos., in south-west Colorado; other deposits are met with near Coal Creek in Rio Blanco Co. and Skull Creek in Routt Co. in north-west Colorado. Most of these deposits are in Jurassic (La Plata) sandstone, but some of those in the N.W. are in sandstones of Cretaceous age. They have been mined at several spots, and a plant for the extraction of uranium and vanadium salts has been erected near Cedar in San Miguel Co., Colorado. Owing, however, to difficulties of transport and to the low grade of the sandstone ore, no great measure of success has yet been attained. An average sample of marketed ore assayed U_3O_8 11·49 p.c. and V_2O_5 6·40 p.c.

In South Australia, at Radium Hill, near Olary, carnotite occurs in films on the joint-planes of a large deposit of ilmenite, rutile, and magnetite.

A closely allied mineral, named *ferganite* (I. A. Antipov, 1908; Abstr. in Jahrb. Min. 1909, ii. 38), is a hydrated vanadate of uranium and lithium. It occurs, together with other uranium minerals, in prov. Fergana in Russian Turkestan.

L. J. S.

CARO'S ACID. Monopersulphuric acid (*v.* SULPHUR).

CAROBS. Specimens of commercial carobs are found to possess the following percentage composition: water, 9–13; nitrogenous compounds, 5–7; cellulose, 8–12; fat, less than 1; ash, 2; sugars (dextrose and sucrose in variable proportions), 30–43; phosphoric oxide, 0·16–0·24 (Balland, J. Pharm. Chim. 1904, [6] 19, 569).

CARONE *v.* KETONES.

CARONY BARK *v.* CUSPARIA BARK.

CAROUBIN and **CAROUBINOSE.** According to Effront (Compt. rend. 1897, 125, 38), the seeds of *Ceratonia siliqua*, used as a cattle food in Portugal, contain a carbohydrate, *caroubin*, which, when purified, forms a white spongy

friable mass, giving with water a thick syrup or jelly. By hydrolysis, it yields *Caroubinose* ($C_6H_{12}O_6$), which has about the same reducing power as dextrose. Is probably identical with mannose (Van Ekenstein, Compt. rend. 125, 197) (*v.* CARBOHYDRATES).

CARRAGEEN. *Carageen, Carragheen,* or *Carragaheen.* (Fr. *Gaëmen.*) *Irish or Pearl moss.* An alga (*Chondrus crispus*) found on all the western coasts of Europe and on the east coast of North America. In Ireland it is collected, dried, and bleached in the sun. Found in commerce as flat, dry, yellow-white pieces 2 to 3 inches long, usually branching, of a very faint odour and mucilaginous taste, swelling in water like gelatine. Almost completely soluble in boiling water; the solution sets to a jelly on cooling. Contains a high percentage of nitrogen, and is of value as a food in diseases of lungs and general weakness, usually taken dissolved in hot milk. It has also been applied as a size and for stiffening silk, also occasionally in making jellies.

Sometimes found largely adulterated with *Gigartina mamillosa,* which is less valuable and recognised by its stalked fruits and channelled stem (*v.* ALGÆ).

CARRAWAY OIL *v.* OILS, ESSENTIAL.

CARRIAGE VARNISH *v.* VARNISH.

CARROT, the tap root of *Daucus carota* (Linn.). Several varieties exist, and the roots are employed as cattle food and as a table vegetable. Kellner gives as the average composition:

Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
87·0	1·2	0·2	9·3	1·3	1·0

According to American analyses, the average composition of the edible portion, as a table vegetable, is:

Water	Protein	Fat	Sol. carbohydrates Fibre	Ash
88·2	1·1	0·4	9·2	1·1

The Belgian white carrot is often used for the field crop, whilst the red carrot is preferred for table purposes. The reddish colouring matter of the carrot, *carrotene,* is sometimes used in colouring butter and cheese. It has the composition $C_{40}H_{56}$, and can be obtained by rasping the roots, precipitating the juice with lead acetate, with which the carrotene forms a lake. This is dried and extracted with carbon disulphide. The solution is evaporated to dryness and repeatedly extracted with cold petroleum spirit in order to remove cholesterol. The residue is then dissolved in carbon disulphide, from which the carrotene is precipitated by the addition of alcohol. It can then be recrystallised from benzene in the form of rhombic plates with a metallic lustre, blue by reflected, orange-red by transmitted light. The cholesterol obtained from carrots has the composition $C_{26}H_{44}O$, and melts at 136·5°, and is apparently the substance previously described as hydrocarrotene (Arnaud, Compt. rend. 102, 1319) (*v.* CARROTENE).

As a farm crop, carrots are particularly valued for horses and dairy stock. They are best grown on light land, free from stones and weeds and well tilled. H. I.

CARROT GUM *v.* GUMS.

CARROTENE. The colouring matter of *Daucus carota* (Linn.). Found also in the leaves of plants to the extent of 0·1 to 0·2 p.c. (Arnaud, Compt. rend. 1890, 109, 911) in full vegetation, and to a slight extent in etiolated leaves (Immendorf, Chem. Zentr. 1890, i. 163), and in the tomato. It forms the colouring matter of yellow and orange pollen; the oily drops on the surface of the pollen of *Verbascum thapsiforma* contain not less than 6·6 p.c. of carrotene; and in the animal kingdom it occurs as the colouring matter in *Diaptomus bacillifer* (Blanchard, Compt. rend. 1890, 110, 292). It can also be extracted from stinging-nettle leaves with light petroleum (Willstätter and Mieg, Annalen, 1907, 355, 1). Carrotene crystallises in copper-coloured leaflets which appear red by transmitted light, and have m.p. 167·8°. It is insoluble in water, readily soluble in carbon disulphide or benzene, sparingly so in alcohol, ether, petroleum, or chloroform. Carrotene is able to decompose carbon dioxide with formation of oxygen, and this probably explains why etiolated leaves can, under certain conditions, generate oxygen (Kohl, Chem. Zentr. 1906, ii. 442).

Carrotene is an unsaturated hydrocarbon having the formula $C_{40}H_{56}$ (Willstätter and Mieg, *l.c.*); it combines with iodine to form the *iodide* $C_{40}H_{56}I_2$, which crystallises in rosettes of dark-violet prisms, and decomposes at 140°–170°; and the *iodide* $C_{40}H_{56}I_8$, which forms dark-violet plates and decomposes at 136°–137°. The *bromo-* compound $C_{40}H_{56}Br_{22}$ decomposes at 171°–174° (Willstätter and Escher, Zeitsch. physiol. Chem. 1910, 64, 47). Carrotene dissolves slowly in concentrated sulphuric acid, forming an indigo-blue solution from which the hydrocarbon is precipitated in green flakes on the addition of water; it absorbs oxygen to the extent of 34·3 p.c. of its weight, yielding a colourless substance. When carrotene is oxidised with a small amount of acetic acid solution of chromic anhydride, and the temperature kept below 30°–40°, an *oil* $C_{40}H_{56}O_8$ or $C_{40}H_{60}O_8$ is obtained, and this does not solidify at −10° (Euler and Nordenson, Zeitsch. physiol. Chem. 1908, 56, 223).

CARVACROL *v.* CAMPHORS; also OILS, ESSENTIAL.

CARVEOL *v.* CAMPHORS.

CARVOL *v.* CAMPHORS; also OILS, ESSENTIAL.

CARVONE *v.* KETONES.

CASCARA SAGRADA. The dried bark of the *Rhamnus Purshiana* (D. C.), a small species of thorn tree inhabiting the Pacific slopes of the Rocky Mountains. (For botanical characters, *see* Hooker (Flora Bor. Amer. 43), Prescott (Amer. J. Pharm. 1879, 165), Möller (Pharm. J. [3] 14, 467); Moss (*ibid.* [3] 649, 19).) Cascara sagrada has been long known as a cathartic to the Indians and trappers of California; but it has only recently been introduced into American and European medicine. Its physiological action is similar to the other and better-known *Rhamnus frangula* (Linn.), but the *Pursahian* is the more esteemed. (*Cf.* Kennedy, Amer. J. Pharm. 1885, 496.)

Cascara bark has been examined by Prescott (*ibid.* 1879, 165); Limousin (J. Pharm. Chim. [5] 6, 80); Wenzell (Pharm. Rundsch. 1886, 79); Meier and Webber (Pharm. J. [3] 18, 804); Schwabe (Arch. Pharm. 226, 569); Zeig (Pharm. J. [3] 20, 173); Le Prince (Compt. rend. 115,

286), Dohme and Engelhardt (Amer. Chem. J. 20, 534); but the statements made regarding it are very conflicting, for a summary of which *see* Jowett (Rep. Amer. Pharm. Assoc. 1904, 1), who has also made an exhaustive examination of the bark. He has confirmed the presence of *emodin* together with a small proportion of an isomeric substance which may be identical with the *iso-emodin* obtained from *Rhamnus frangula* by Thorpe and Miller (Chem. Soc. Trans. 61, 6). Glucose is also present, and a substance which, on treatment with acid, yields syringic acid. No evidence was obtained of the existence of chrysophanic acid or chrysarobin or of glucosides yielding on hydrolysis emodin, chrysophanic acid, or rhamnetin. The cascarine of Le Prince and the purshianin of Dohme and Engelhardt are probably impure products. Emodin is not the active principle of the drug, and no clue could be obtained as to the nature of this principle. Cascara bark contains about 2 p.c. of fat and a small proportion of a volatile oil. The constituents of *R. Californicus* appear to differ very little from those of *R. Purshiana*. (For methods for the estimation of the active constituents of Cascara sagrada, *see* Warin (J. Pharm. chim. [6] 22, 12).) A. S.

CASCARILLA BARK. The bark of *Croton Cascarilla* (Benn), or *C. Eluteria* (Benn), or 'seaside balsam,' a euphorbiaceous tree growing in the West Indies.

Duval obtained from it a substance, *cascarilline* $C_{12}H_{18}O_4$, which Alessandri (Arch. Pharm. 220, 690) also isolated by extracting the bark with oxalic acid and precipitating the extract with ammonia. This substance dissolves in hydrochloric acid, producing a rose-coloured solution, which changes through purplish-red, violet, and green to a sky-blue without the addition of water. Boehm (Pharm. J. [3] 16, 366) finds in addition an alkaloid closely allied to cholin. An examination of this alkaloid by Naylor (Pharm. J. 59, 279) indicates that it is betaine. A. S.

CASCARILLA OIL *v.* OILS, ESSENTIAL.

CASEIN. Casein occurs in the milk of mammals, and is the principal protein of cow's milk, which, up to the present, is its only commercial source. Cow's milk contains, on an average, about 3 p.c. of casein, which exists in a suspended or colloidal condition, probably as a lime compound in combination with calcium phosphate, giving the milk its opaque appearance. This can easily be proved by allowing the milk to pass through a filter of unglazed porcelain, when a white mass of casein and fat will be found on the surface of the filter, and the filtrate will contain the lactose, soluble albumen, and soluble salts of milk.

Preparation of pure casein. Separated milk is diluted to about five times its volume with water and sufficient acetic acid added to give 0·1 p.c. of acid in the solution. The casein is precipitated, carrying down with it the fat. The curd is washed about ten times by decantation, collected on a cloth filter, washed, and pressed as dry as possible. It is then dissolved in the least quantity of ammonia, and filtered. The filtrate is precipitated with acetic acid, washed, and redissolved in ammonia. This process is repeated three or four times. The curd is then rubbed up in a mortar several times with 80 p.c. alcohol, and finally with absolute alcohol. It is next similarly treated with ether, and extracted with ether in a Soxhlet apparatus, and the casein finally dried at 100°C.

Properties.—Thus prepared, casein is a white, amorphous body without taste or smell. It is very sparingly soluble in water, and quite insoluble in alcohol and ether. Its most probable percentage composition is: C, 53·13; H, 7·06; N, 15·78; P, 0·86; O, 22·40; S, 0·77.

Casein is a phospho-protein. Its molecular weight is stated to be about 1135. It is a weak dibasic acid, forming acid and neutral salts with alkalis. In dilute alkaline solutions, it has a lævo-rotary action on polarised light. At the ordinary temperature, 1 gram of casein combines with 9 c.c. of N/10 hydrates or carbonates of alkalis, and with nearly 7 c.c. decinormal solutions of common acids. It is soluble in caustic alkalis, and in the carbonates, bicarbonates, phosphates, &c., of the alkali metals, and is precipitated unchanged by addition of sufficient acid to neutralise the alkali.

Casein is soluble in strong hydrochloric acid, giving a fine violet colour, and is also soluble in dilute hydrochloric acid containing 0·2 p.c. of the fuming acid, but is insoluble in 2 or 3 p.c. acid.

Preparation of industrial casein. There are many methods of preparing casein, but on the large scale these are generally limited to three:

(1) Precipitation by means of acid—usually sulphuric, though acetic, phosphoric, lactic, hydrochloric, &c., are also employed.

(2) Curdling by means of rennet.

(3) Curdling by 'self-souring.'

A very interesting method of preparation is by means of electricity, but so far this does not seem to have progressed beyond the laboratory stage. The method, however, will be described later. Whichever method be employed, the first essential is a machine-separated milk, containing the smallest possible quantity of fat. Milk taken from cows shortly after calving, and containing colostrum, is unsuited for casein manufacture. It gives a soft curd which squeezes through the filter cloths, and holds a great deal of water. It has sometimes been found necessary to throw away a whole batch as the curd has been quite unworkable.

Also, if the milk has been pasteurised at such a high temperature that some of the lact-albumin becomes insoluble, the curd will give a great deal of trouble.

The milk from the separators is run into a tank of suitable dimensions, and brought to the required temperature by means of steam.

Precipitation by sulphuric acid.—The requisite quantity of sulphuric acid, previously diluted with water in a wooden or enamelled iron bucket, is then introduced, and the whole well agitated, when the milk will gradually lose its opaque appearance and become clear with separation of the curd. As soon as the whey is yellow and transparent, the agitation is stopped, and the curd falls to the bottom of the tank. The whey is run off, the curd allowed to drain and washed with cold water until all the whey has been separated. The bulk of the water is then removed by means of a suitable press or by a centrifugal machine.

Curdling with rennet.—The amount of rennet required depends upon the acidity of the milk and the temperature. The more acid the milk and the nearer the temperature approaches 106°F., the less is the rennet required. At 118·5°F. and at 86°F., the curdling power of rennet is only about 70 p.c. of that at 106°F.

If the acidity of the milk be 15°, about 2½ oz. rennet should curdle 100 gallons of milk in about ¼ hour.[1] When the acidity reaches 30°, half this quantity will suffice. The requisite quantity of rennet is diluted with water and thoroughly stirred into the milk at a temperature of about 106°F. The milk is then allowed to rest until it has 'set' like a junket. The mass is cut up into small cubes by special knives, and then agitated gently at first, and afterwards vigorously while being very slowly heated up to about 120°F. by means of free steam or a steam-jacket. The curd will then be in hard grains or nodules at the bottom of the tank. The whey is rapidly run off, the curd washed well with cold water, and pressed.

Curdling by 'self-souring.'—When milk is exposed to the air, it becomes acid. This change is effected by the *Bacillus acidi lactici*, which converts the lactose into lactic acid. When sufficient acid has been formed, the curd separates from the whey. On the large scale, the separated milk is run into a tank, the temperature brought to and maintained at about 98°F., at which point the growth of the bacilli is most rapid. After some hours, according to the freshness of the milk, a sour smell will be noticed and the milk will begin to curdle. When the right point has been reached, steam is turned on and the mass agitated in order to make the curd firm, and in a suitable condition for washing and pressing. The whey is then run off and the curd finished in the usual manner.

Drying of the curd.—When as much moisture as possible has been removed from the curd, it is broken up and dried. This may be effected either by spreading on trays in heated drying-rooms fitted with ventilating appliances to facilitate the removal of the moisture, or in a drying cylinder heated from inside or outside or both, and rotated to keep the contents in constant motion. Another method of drying the curd is by means of a Passburg vacuum drier, consisting of a cast or wrought-iron case, which can be hermetically closed by doors. A vacuum is produced by an air pump, and the moisture is vapourised at a low temperature so that drying is soon effected.

Whatever process be adopted, the temperature must be carefully watched, as a few degrees too much heat will 'burn' the casein to a rich brown colour, and if the temperature be too low the curd will take a long time to dry, and may become sour and mouldy.

The dry casein is then ground to a fine powder, when it is ready for the market.

Curdling by electricity.—Although this process is so far not a commercial one, it is sufficiently interesting to warrant a short description. The milk is heated to 120°F., and a porous cell, containing dilute milk, is placed in the centre. A current of electricity of sufficient tension is passed, and the soluble elements, the phosphates in particular, are decomposed. The anode is placed in the milk and the cathode in the porous cell. Phosphoric acid is then liberated in the milk, and causes the precipitation of the casein, while the liquid in the porous cell becomes strongly alkaline. The chief difficulty lies in the choice of electrodes—the cathode in the porous cell can be carbon, but the anode must be of platinum, which makes the original cost very heavy. Any of the common metals are attacked in a very short time, and carbon throws off small particles which cause the precipitated curd to become black. It is, of course, possible to have both electrodes of carbon in porous cells, but it is found that the curd soon fills up the pores and the action becomes very slow.

Properties.—Industrial casein, prepared with sulphuric acid, will dissolve in the following quantities of alkalis or alkaline salts, though larger quantities are always used in the various industries :—

	Per cent.
Sodium bicarbonate . .	3½
Sodium carbonate . .	2¾
Sodium hydroxide . .	1¾
Sodium silicate 140°Tw. .	10
Sodium arsenate . . .	20
Sodium sulphite . . .	9
Strontium hydrate . .	20
Trisodium phosphate . .	8
Ammonia, ·880 . . .	2½
Sodium tungstate . .	12½
Borax	9½

Solutions of the hydroxides of potassium, sodium, lithium, and ammonium of equal concentration, dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly; strontium hydroxide dissolves it most rapidly, calcium hydroxide more slowly, and barium hydroxide more slowly still.

Rennet casein is insoluble in carbonate and bicarbonate of soda, partly soluble in borax and ammonia, and soluble in trisodium phosphate and lime.

Its solution in alkalis does not coagulate on heating, but is precipitated by acids and many metallic salts. When acted on by formaldehyde and certain other bodies, casein is rendered insoluble. Advantage is taken of this fact in various industries to give a waterproof coating of casein.

Pure casein contains only a very small amount of ash, but industrial casein may contain up to about 7 p.c. or 8 p.c.—rennet-prepared casein containing the most, and 'self-soured' casein the least.

Uses of casein. Casein is employed in a large number of industries, and its use is increasing every year, in fact, there are but few industries in which casein, in some shape or form, is not or cannot be employed with advantage.

The greater quantity of imported casein, the value of which, in 1909, was about 50,000*l.*, comes from the Argentine. Large quantities also are received from France and Germany, and smaller quantities from Holland, Belgium, and the United States.

[1] The 'degree of acidity' of milk is the number of c.c. of *N*/10-NaOH sol. required to neutralise the acid in 100 c.c.

Casein is used in paste and dry distempers; in cardboard manufacture, paper glazing, leather dressing, soap manufacture, cotton sizing, dressing for textiles, finishing, waterproofing, calico printing, cask glazing; imitation bone, ivory, tortoiseshell, amber, ebony, &c.; picture mouldings, sealing for bottles, cabinet and pianoforte making, emulsions, fining wines, boot polishes, waterproof cements, polishes, films, diabetic and protein foods.

Alimentary casein. Some of the best-known food preparations of casein are:

Plasmon.—This is a cream-coloured powder, somewhat coarse in texture. It is a soda compound of casein, and is partially soluble in water. It contains nearly 2 p.c. of lactose (milk-sugar) and about 70 p.c. of proteins.

Sanagen.—A fine white powder, completely soluble in water. It is a compound of casein with about 5% of sodium glycerophosphate made by a special process. It contains about 76–78 p.c. proteins, and is practically free from lactose, and so is specially recommended for diabetic patients.

Sanatogen.—A white powder soluble in water. It consists of casein with about 5 p.c. of sodium glycerophosphate, and is free from fat and lactose.

Dr. Reigel's milk protein.—A soda compound of casein, soluble in water. According to the patent specification, the curd is precipitated from the milk by means of ethyl-sulphuric acid.

Eucasein.—A casein-ammonia compound, soluble in water.

Nutrose.—A soda compound of casein.

Casein solids. *Galalith.*—Insoluble casein, treated with formaldehyde and subjected to heavy pressure, gives plates of great hardness, and by blending pigments with the casein, imitations of bone, ivory, ebonite, &c., are obtained. The products are known as *Galalith* (from the Greek *gala*, milk, and *lithos*, stone). The following articles are made from galalith: brush-backs, combs, cigar and cigarette holders, penholders, electrical fittings, umbrella and stick handles, buttons, dominoes, &c. Being uninflammable, casein possesses great advantages over celluloid. It is a bad conductor of electricity, and is therefore suitable for electrical fittings. A plate of galalith $\frac{1}{8}$ inch thick, is impervious to a current of 16,000 volts.

Lactoform.—This is a patented preparation of casein resembling horn, giving, according to the specification, a hard and tough article which does not swell or materially soften when immersed in water. It is prepared by adding various salts to solutions of casein; thus, by adding a solution of lead acetate to a solution of casein, a coagulum is produced from which lactoform, resembling *horn*, may be obtained, while to manufacture a substitute for ivory, carbonate of soda is added to the casein solution and precipitated by sugar of lead, thus forming carbonate of lead in the mass obtained. By the use of chromium compounds, bluish-green, also yellow and orange lactoform, is obtainable; by the action of iron, rust-coloured, and in combination with tannic acid, slate and black-coloured, lactoform may be produced. These are merely intermediate products, and are not claimed as a new invention, but are converted into lactoform by treatment with formaldehyde.

For *glues* and *sizes*, casein is dissolved in borax, soda, or ammonia, and the resulting coating may afterwards be rendered insoluble by formaldehyde, or the casein may be dissolved in lime, which will give a waterproof coating when dry.

Films.—Schmidt has patented a process for making casein films as follows: 100 grams of casein are dissolved by heating in 1 litre of water containing 8 grams of 25 p.c. hydrochloric acid; 10 grams of 40 p.c. formaldehyde and a small quantity of glycerol are added, and the solution poured on glass plates to dry. He states that films made from alkaline solutions of casein are not impermeable to moisture.

Schmidt patents the following process: 100 grams of casein and 1·5 grams caustic of soda are dissolved in 1 litre of water, to which are added about 15 grams of a 40 p.c. solution of formaldehyde; or 100 grams of casein and 10 c.c. of a 10 p.c. solution of ammonia are dissolved in 2 litres of water, to which are added about 30 grams of a 40 p.c. solution of formaldehyde. Either of these he states, gives insoluble films on drying, which may be used for photography, surgical bandages, paper-coating, &c.

Buss, in his patent for photographic films, proceeds as follows: 500 to 700 grams dry casein are heated with 9 litres of water to 35° or 50°, mixed with 250 grams of citric acid dissolved in 1 litre of water, and the heating continued until the whole has dissolved. Then 100 or 200 grams of glycerol are added, and the liquid filtered. It is applied by machine to plain or baryta paper, and allowed to dry. It is next rendered insoluble by being drawn through a 5 or 7 p.c. solution of ammonium or sodium chloride, and finally sensitised in a silver nitrate bath, ranging between 4 and 12 p.c. in strength.

Sealing for bottles.—For this purpose, Joirgnot has patented the following preparation: Casein is treated with a hot aqueous solution of sodium phosphate, ammonium fluoride and glycerol, the whole being then heated in the water-bath until it is homogeneous and viscous. This product is employed for sealing bottles of metal, glass, porcelain, &c., by applying it in a warm state to the edge of the vessel or cover, and then treating it with formaldehyde.

Fining of wines.—For this purpose, a readily soluble sodium compound of casein is used. It is dissolved in 10 or 20 parts of water, the 5 p.c. solution effecting a somewhat slower though more complete clarification. The casein compound has the advantage that it is very much cheaper than albumen, and is free from all flavour such as is found in even the purest gelatin. Moreover, if in fining wines with white of egg, albumin or gelatin, too large an excess in proportion to the tannin be used, this excess remains in solution, and may lead to turbidity and alteration in the wine; whereas the casein, even when added in considerable excess, is completely eliminated, being coagulated by the acid in the wine.

Casein water-paints.—Casein in fine powder is intimately mixed with sifted slaked lime and incorporated with the pigments. The proportion of lime to casein is very important: if too little lime be used, the mixture will, after a short time, especially if exposed to air, become insoluble in water; and if too much lime be used, adverse results will follow. The brushes will be

rotted and the paint will be liable to flake off. The next matter of importance is the proportion of lime and casein to be incorporated with the pigment. If too little be used, the paint will dust off and will not stand washing; and if too much be used, the coating will be brittle and flake off.

In selecting the pigments, it is necessary to employ only those which are unaffected by lime. The most suitable are:

For White.	Whiting, China clay, zinc oxide.
„ Yellow.	Ochre, Hansa yellow, naphthol yellow, chrome yellow.
„ Brown.	Umber, sienna.
„ Black.	Carbon blacks.
„ Red.	Oxides, lithol red.
„ Blue.	Ultramarine.
„ Green.	Green earth, ultramarine green, lime green.

The ingredients must be thoroughly incorporated and kept in air-tight packages. The paint is prepared by mixing the powder with cold water, and is ready for use in a few minutes. When thoroughly dry, the surface is washable.

L. M. N.

CASHEW GUM *v.* GUMS.

CASSAVA. The root of *Manihot palmata* (Muell.), 'sweet cassava;' or of *Manihot utilissima* (Pohl), 'bitter cassava.' These plants are widely cultivated in the tropics for the sake of their starchy edible roots. From them the substance tapioca is prepared. The starch is also known as mandioc starch, Brazilian, Bahia, Rio or Para arrowroot, and by other names.

The grains of starch are grouped in twos, threes, or fours; the separate grains have usually one or two flat surfaces, but, on the whole, are rounded and show delicate concentric striations and a distinct hilum.

Cassava root contains a volatile poisonous substance (Fermin, 1764), which proved to be hydrocyanic acid (Boutron-Charlard, 1836, and Francis, Analyst, 1878, 2, 4). The latter observer found 0·0168 p.c. of prussic acid in sweet cassava root and 0·0275 p.c. in the bitter root. He found 59·4 p.c. and 61·4 p.c. water in the roots, and about 30 p.c. of starch.

Leuscher (Zeitsch. öffentl. Chem. 1902, 8, 10), as the mean of six analyses of the fresh root, found:

Water	Protein	Fat	Starch	Sugar	Crude fibre	Ash
70·25	1·12	0·41	21·44	5·13	1·11	0·54

He states that the yield, on well-irrigated land, may amount to 15 or 16 tons per acre.

Tapioca is made from the starch of cassava by stirring the damp product on a hot iron plate until it agglomerates into the irregular, spherical masses familiar as tapioca. By this treatment, many of the starch grains become changed, being converted into shapeless, translucent masses.

According to American analyses (Wiley, Bull. 13, U.S. Dept. of Agric. Div. of Chem. 1898), tapioca contains—

Water	Protein	Fat	Carbohydrates	Fibre	Ash
11·23	0·37	0·03	88·16	0·12	0·09

Owing to the exceptionally low demands of cassava for mineral matter, it has been recommended as a crop particularly well adapted for cultivation on poor sandy soils, as it feeds very largely upon air and water (Ewell and Wiley, Amer. Chem. J. 1893, 15, 285). H. I.

CASSEL EARTH or **VANDYKE BROWN** *v.* PIGMENTS.

CASSEL YELLOW. *Lead oxychloride.* A pigment also known as *Turner's Yellow, Montpelier Yellow, Mineral Yellow,* and *Patent Yellow.*

CASSELMAN'S GREEN. A pigment made by mixing boiling solutions of copper sulphate and an alkaline acetate.

CASSIA. The bark of *Cinnamomum cassia* (Blume), a tree belonging to the order *Lauraceæ* or true laurels. It is grown in China, Java, &c. *C. cassia* furnishes a bark which is much like cinnamon [*C. zeylanicum* (Nees)], but thicker, coarser, stronger, less delicate in flavour, and cheaper; hence it is frequently used to adulterate cinnamon. The bark is stripped off the branches, when it rolls up in the form of quills. It is said to be preferred to cinnamon itself by some chocolate makers on account of its stronger flavour. The unopened flower-buds are also sold under the name of 'cassia-buds,' and possess similar properties to the bark. Other species of the genus afford aromatic barks, *e.g. C. culilawan* (Blume), native of Malaya and China, the bark of which has a flavour of cloves; *C. tamala* (Nees), which occurs in sub-Himalayan India as far as Burma, and provides a bark that is used as a substitute for or adulterant of true cinnamon; *C. Burmanni* (Blume) is the source of the bark exported from Sumatra. The bark known as clove-cassia is obtained from *Dicypellium caryophyllatum* (Nees), which is also a tree of the laurel family growing in Brazil.

The employment of cassia as a sophisticant of the more esteemed and more costly bark of cinnamon when in the ground state may usually be detected by adding tincture of iodine to a decoction of the powder; when, since cassia contains more starch than cinnamon, the substance will turn blue; but, where inferior qualities of the true cinnamon have been examined, their constitution has approached that of the coarser bark of cassia, and this test has proved uncertain (*cf.* O. Hehner, Analyst, 1879, 225–228).

Cassia bark is thicker, redder, stronger to the taste than cinnamon. The powder under the microscope exhibits a general resemblance to cinnamon, but it will be seen that cassia differs from cinnamon in its coarser structure, and especially in the greater size and number of its starch corpuscles.

Cassia yields by distillation an essential oil largely used in perfumery, especially for producing the scent in brown Windsor soap (*v.* OILS, ESSENTIAL).

CASSIA OIL *v.* OILS, ESSENTIAL.

CASSIA TORA (Linn.) or **TAGEREY-VEREY.** This plant produces grains known in the East Indies, Arabia, and Japan as *Tora,* but which are known in Pondicherry and other parts of Hindostan as *Tagerey-verey.* It is regularly used as a component of the indigo vat in dyeing, apparently serving the same purpose as the bran-madder or molasses used in Europe.

The native dyers use the *Tagerey-verey* in the following manner. To dye about 200 yards of cloth, 11½ lbs. of the grain are steeped in from

5 to 6 gallons of cold water, and then boiled for four hours. The grains are swollen and softened by this treatment, and the water becomes thick and gummy. The whole of this is added to the indigo vat, and after standing for fifteen hours, the vat is ready to dye.

CASSITERITE or **TIN-STONE.** Native tin oxide SnO_2, containing 78·6 p.c. of tin, and practically the only ore of the metal. It varies much in appearance—the colour ranges from white to black, being usually dark brown—and its most characteristic feature is its high sp.gr. of 6·8–7·1; hardness, 6–7. Crystals are tetragonal, with very characteristic knee-shaped twins; their faces are often very brilliant with an adamantine lustre. Crystals are, however, not very common, the mineral being more frequently found as disseminated grains and water-worn pebbles. Veins of tin ore usually occur at the junction of granitic masses and slates, and the ore also impregnates the rocks bordering the veins. Such ores are known as *vein-tin*, to distinguish them from the *stream-tin* of alluvial deposits. A compact variety with a radially fibrous and concentric structure and sometimes a botryoidal surface is known as *wood-tin*. The ore as prepared for market is known as *black-tin*, and in South America as *barilla*. The principal tin-producing countries are the Federated Malay States, the islands of Banka and Billiton in the Dutch East Indies, Australia (Queensland, New South Wales, Western Australia), Tasmania, Bolivia, Cornwall, and more recently South Africa (Transvaal and Swaziland), and Northern Nigeria. The production of tin ore amounts to about 100,000 tons per annum. L. J. S.

CASSIUS, PURPLE OF, *v.* GOLD.

CASTILE SOAP *v.* SOAP.

CASTOR or **CASTOREUM.** (*Bibergeil*, Ger.) A name given to a secretion of the beaver (*Castor fiber*), contained in pear-shaped cellular sacs (found near the genital organs of the male and female animal), which are cut off and dried, to prevent the skin being affected by water. It is a substance analogous to civet and musk, and is of the consistency of thick honey and unctuous to the touch. The interior substance is solid, of a dark-brown or black colour. It has a faint smell, softens when heated, but becomes brittle when cold. When chewed, it sticks to the teeth like wax. It has a bitter acrid taste, and a fœtid, penetrating smell. Its fracture is shining, and when the substance is genuine it shows fragments of membrane indicating organic structure.

Three varieties are said to exist, the Russian, Bavarian, and American or Canadian, the first-named variety containing about 2 p.c. of the volatile oil, while the last contains only 1 p.c.

Wöhler obtained phenic and benzoic acids and salicine from it. Lehmann found bile in a fresh sample together with alkaline urates, sebates, and an albuminoid substance. Laugier, Brandes, Batka, Bouillon, Lagrange, and Hildebrant have also examined it. By extracting it with six times its weight of alcohol a colourless substance, *castorin*, has been isolated. Used in medicine and perfumery.

CASTOR OIL is obtained from the seeds of *Ricinus communis* (Linn.).

The plant appears to be indigenous to Africa (Egypt), but has been transplanted to India at a very early stage of history, so that some writers consider the plant indigenous to India itself. The plant grows in enormous quantities in all tropical and sub-tropical countries, and is even found wild to-day in South America, notably in Paraguay and the Argentine.

The most important sources of castor seed are East India, Java, the Mediterranean countries, Mexico, and the United States of America. By far the largest producer is East India.

The seeds consist of 20 p.c. of husks, which are rich in mineral matter, but contain no oil, and 80 p.c. of kernels, forming a white, softish mass. The whole seeds contain a toxic principle —'ricine' or ricinine. The kernels contain a powerful fat-hydrolysing enzyme, which can be made use of on a manufacturing scale for hydrolysing oils and fats for soap-making purposes. The seeds contain 46 to 53 p.c. of oil. The oil is produced on a large scale either by expression or extraction. For the production of best quality oil—for medicinal purposes—the seeds are decorticated before being expressed. The press-cake is subjected to a second and third expression, but the oils so obtained are unfit for medicinal use, and are employed for technical purposes (soap-making, Turkey-red oil, and lubricating oils). The cakes retain the poisonous alkaloid, and are therefore unfit for feeding purposes. Although it is stated that by washing the cakes with 6 or 7 times their amount of a 10 p.c. sodium chloride solution, they can be freed from the alkaloid, no castor cake is actually used for feeding cattle, but applied exclusively to manuring the land. The extracted oil is only used for technical purposes.

Crude castor oil is refined by steaming the oil, whereby the albuminous substances are coagulated, so that they can be removed by filtering.

Castor oil is a colourless or pale-greenish oil, having a taste at first mild, then harsh; this harsh taste is more pronounced in American then in Italian or French oils. The oil differs from all other fatty oils by its high specific gravity, viz. 0·960. Contrary to older statements, the oil does not dry, even when exposed to the atmosphere in thin layers.

Castor oil is strongly dextro-rotatory; the optical activity is due to the presence of ricinoleic acid.

The chief constituent of castor oil is the triglyceride of ricinoleic acid, both isomerides ricinoleic and *iso*ricinoleic acid being comprised under this term; in addition thereto, castor oil contains a small proportion of glycerides of a natural dihydroxystearic acid and of stearic acid. Palmitin and oleïn are absent.

Owing to the presence of triricinoleïn, castor oil is distinguished from all other fatty oils by its high 'acetyl value' (*see* OILS and FATS). Castor oil further differs from all other fatty oils by its ready miscibility with absolute alcohol and glacial acetic acid, as also by its insolubility in large quantities of petroleum ether, kerosene, and high-boiling paraffin oils. The oil gives a homogeneous solution with an *equal* measure of light petroleum, or one volume and a half of kerosene or paraffin oil; if more of the solvents is used, the excess will float on the top of the mixture. If castor oil be mixed with a

small quantity of another fatty oil, this characteristic insolubility in petroleum distillates is lost.

On subjecting castor oil to destructive distillation (as in the preparation of 'cognac oil'), undecylenic acid and œnanthaldehyde distil over, whilst the residue solidifies to a very bulky, spongy, indiarubber-like mass, for which a solvent has not yet been found. This residue appears to consist of the anhydride of triundecenoic acid. By heating castor oil for 10 hours at a temperature of 260°–300° under a pressure of 4–6 atmospheres, the oil becomes miscible with mineral oils. J. L.

CASTOR OIL SEEDS or CASTOR BEANS. The seed of *Ricinus communis*, a plant which grows as a tree in warm countries, attaining a height of 30 or 40 feet, but which in cooler climates is only an annual shrub.

The following is an analysis of Indian seeds (Halenke and Kling, Landw. Versuch. St. 1906, 64, 51):—

	Water	Protein	Oil	Sol. carbohydrates	Fibre	Ash
Kernels, 70 p.c.	3·60	23·43	66·02	4·01	0·70	2·24
Husk, 30 p.c.	8·76	4·76	0·98	32·92	48·69	3·89
Whole seed	5·14	17·88	46·65	12·61	14·99	2·73

In many varieties the proportion of husk is much lower, sometimes down to 20 p.c.

Of the total 'protein,' 22·62 p.c., 4·18 p.c., and 17·13 p.c. respectively, are true albuminoids, whilst of the carbohydrates, 0·89 p.c., 15·63 p.c., and 5·29 p.c. respectively, are pentosans.

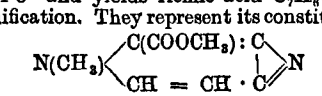
The ash of castor seeds was analysed by Thoms (1890)—

Sand, etc.	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	Cl
0·30	19·59	5·65	17·08	10·53	14·30	1·88	23·67	6·01	0·29

Castor seeds are very poisonous. Cornevin found the following were the toxic doses in grammes per kilogram of body-weight. Horses, oxen, sheep and dogs, 3; pigs about 5–6; hens about 40.

The poisonous constituent was believed to be *ricinine* by Soane (Chem. Zentr. 1895, i. 853), but is now known to be *ricin*, an albumin, which, with two non-toxic substances—a proteose and a globulin—constitute the proteids of the seeds (Osborne and Mendel, Proc. Amer. Physiol. Soc. 1903, 36).

Ricinine, according to Macquenne and Philippe (Compt. rend. 1904, 138, 506 and 139, 840), has the composition $C_8H_8O_2N_2$; it melts at 201·5° and yields ricinic acid $C_7H_6O_2N_2$ by saponification. They represent its constitution as



Ricin, the poisonous principle, has been examined by Stillmark (Chem. Soc. Abstr. 1890, 535), Osborne, and others (*l.c.* and Amer. Jour. Physiol. 1905, 14, 259), and Brieger (Chem. Zentr. 1904, i. 1286). It can be extracted from the pressed seeds by a 10 p.c. solution of common salt, from which it is precipitated by magnesium and sodium sulphates.

Ricin agglutinates the red corpuscles of the blood. Osborne found 0·002 milligram per kilogram of body weight sufficient to kill a rabbit when subcutaneously injected. It can be kept for months without deterioration, but loses its poisonous qualities when coagulated by heat, Toxic symptoms do not appear until after a latent period of about 15 hours. Castor seeds also contain an enzyme capable of decomposing fats into glycerol and fatty acids.

Castor seeds are largely used as source of castor oil (*q.v.*). The cake left is rich in protein, and if it were not poisonous, would prove of value as a cattle food. It contains—

Protein	Oil	Soluble carbohydrates	Fibre	Ash
29–34 p.c.	1–4 p.c.	12–18 p.c.	30–40 p.c.	6–9 p.c.

By subjecting the cake to high-pressure steam, the poisonous qualities are said to be destroyed, and cake so prepared may safely be used as a part of the ration of fattening animals. According to Ehrlich, animals may be immunised against the poison by feeding them with very small quantities of the crude cake until they become accustomed to it. The serum from such animals may then be used to immunise others.

Neither of these methods of utilising castor cake appear to have been successful, and, in England, at least, it is rarely or never used for feeding purposes.

The leaves of the castor plant are rich in lime and potash: an analysis by Wayne (Pharm. J. Trans. 1874, 3, 749) gave as the composition of the ash of the leaves:—

CaO	MgO	K_2O	Na_2O	Fe_2O_3	P_2O_5	SO_3	Cl	CO_2	SiO_2
33·4	6·2	27·3	2·1	0·7	6·7	2·9	1·6	16·2	2·4

H. I.

CATALASE *v. Enzymes*, art. FERMENTATION.

CATALYSIS *v.* CHEMICAL AFFINITY.

CATECHIN *v.* CETECHIN.

CATECHOL (*Pyrocatechol* or *Pyrocatechin*, *o-Dihydroxybenzene*, 1 : 2-Phendiol $C_6H_4(OH)_2$, occurs in the leaves of the Virginia creeper (*Ampelopsis hederacea*) (Gorup Besanez, Ber. 1871, 4, 905); in the sap of various kinds of the kino plants (Eisfeldt, *ibid.* 906; Flückiger, Ber. 1872, 5, 1, 47); in crude beet sugar (Lippmann, Ber. 20, 3298; 1893, 26, 3061; J. Soc. Chem. Ind. 1893, 535); in the dry external scales of the onion; in Paglia olive oil (Cauzoneri, Gazz. chim. ital. 27, 3); in the colouring matter of red grapes (Sostegni, Gazz. chim. ital. 32, 17); in Silesian and Westphalian coal (Bornstein, Ber. 1902, 35, 4324); and in the tar water of bituminous shale (D. R. P. 68944, 1892; Ber. 1902, 35, 4325). The catechol complex also exists in certain glucosides (Nedra, J. Soc. Chem. Ind. 1900, 686; Schmidt and Waljaschko, Chem. Zentr. 1901, ii. 121), in a large number of products of vegetable origin; as the sulphate, catechol occurs in the urine of man and herbivorous animals (Müller, Ber. 1874, 7, 1526; Schmiedeberg, Zeitsch. physiol. Chem. 6, 189); it is probably also contained in the cerebro-spinal fluid (Halliburton, J. Phys. Chem. 10, 247).

It is formed in the dry distillation of moritannic acid (Wagner, Annalen, 1850, 76, 351; 80, 316); of catechin (Zwenger, Annalen, 1841, 37, 327); of protocatechuic acid (Strecker, Annalen, 1860, 118, 285), and of all tannins which give a green colouration with iron chloride (Uloth, Annalen, 1859, 111, 215). It is also formed when filter paper is heated to 200° or when starch or sugar is heated to 280° with water (Hoppe Seyler, Ber. 1871, 4, 15) and in many other reactions.

Catechol is prepared by fusing sodium

o-benzene disulphonate (10 parts) with sodium hydroxide (10–15 parts) in an autoclave for 8–10 hours at 280°–300° and pressure of 2–3 atmospheres. The mass is then dissolved in dilute sulphuric acid, neutralised with chalk, evaporated, cooled and filtered. The mother liquor is now heated in an autoclave with 50 p.c. sulphuric acid (10 parts) to 180°–220°. The phenol is removed from the solution so obtained by blowing steam through it; it is then decolourised with animal charcoal, after which the catechol is extracted with ether (Baum, Eng. Pat. 21853; D. R. P. 80817; J. Soc. Chem. Ind. 1894, 879; Ellis, *ibid.* 1897, 674; Frdl. 1894–7, 116). Catechol is also prepared by heating catechol disulphonic acid or the sodium salt with water or mineral acid to 200°–215° for 10–15 hours under pressure (Tobias, D. R. P. 81209, 1894; Frdl. 1894–7, 117); or by treating commercial catechu with water (Gutknecht, Chem. Zeit. 1891, 15, 959); or by diazotising *o*-aminophenol, treating the product with boiling aqueous copper sulphate, and then extracting the catechol with ether (Frdl. 1905–7, 128); or by the distillation of orthobromo- or chlorophenol *in vacuó* or in steam (D. R. P. 76597; Frdl. 1890–4, 845), or by heating with sodium hydroxide (Frdl. 1894–7, 114; D. R. P. 84828). An almost theoretical yield of catechol can be obtained by treating guaiacol with fuming hydriodic acid (Perkin, Chem. Soc. Proc. 1890, 90); or by the interaction of *o*-hydroxybenzaldehyde with aqueous sodium hydroxide in equimolecular proportions; to the sodium salt thus formed, an equimolecular proportion of 2–3 p.c. hydrogen peroxide is then added and the catechol is extracted with a suitable solvent (Dakin, Amer. Chem. J. 1909, 42, 477). Other methods of preparing catechol are described by Cross, Bevan, and Heiberg (Ber. 1900, 33, 2018); Kunzkrause (Ber. 1897, 30, 1620); Meyer (*ibid.* 2569); Hartmann and Gattermann (Ber. 1892, 25, 3532; D. R. P. 70718; Frdl. 1890–4, 52); Gilliard, Monnet and Cartier (D. R. P. 97099; Chem. Zentr. 1898, ii. 521); Messel (D. R. PP. 68944, 60637; Frdl. 1890–4, 844, 846).

Catechol is readily soluble in water, alcohol, ether, benzene, and crystallises from these solvents in prismatic needles or tablets; m.p. 104°; b.p. 245° (Gräbe, Annalen, 1889, 254, 296). Its aqueous solution precipitates metallic silver from silver nitrate solution at ordinary temperature, and with ferric chloride it gives a green colouration, which turns violet on addition of ammonia or sodium acetate (Wislicenus, Annalen, 1896, 291, 174), whilst in the presence of aromatic amino-sulphonic acids the colour changes to red-brown and the test is more delicate than with ferric chloride alone (Bayer, Biochem. Zeitsch. 1909, 20, 178). Unlike its isomeride, resorcinol (metadihydroxybenzene), it is converted into an unstable quinone by the action of silver oxide, and its calcium salt $Ca(C_6H_5O_2)_2$ is precipitated by an ammoniacal solution of calcium chloride (Böttinger, Ber. 1895, 28, Ref. 327). Catechol can be separated from its isomeride by adding antimonyl fluoride to their aqueous solution, when only catechol antimonyl fluoride will be precipitated (Causse, Ann. Chim. Phys. 1898, (vii.) 14, 526, 538).

An alkaline solution of catechol becomes green, then black on exposure to air; catechol is also oxidised to a black insoluble substance by the action of *Catecholase*, a thermostable substance obtained from the young shoots of *Salix purpurea* (Weevers, Proc. K. Akad. Wetensch, Amsterd. 1909, 12, 193). Heated with ammonium carbonate to 140°, catechol yields protocatechuic acid $C_6H_3(OH)_2CO_2H$.

Catechol is used in photography, forming a very efficient developer in the presence of sodium sulphite or tribasic sodium phosphate as accelerator (Eder, J. Chem. Soc. Ind. 1890, 102; Brit. J. Photogr. 1900, 47, 676). It can also be used as the starting-point in the preparation of a large number of valuable derivatives.

Alkali salts of catechol of the general composition $OH{\cdot}C_6H_4{\cdot}OM,C_6H_4(OH)_2$, can be obtained by treating catechol with a solution of the theoretical quantity of alkali hydroxide or of a salt with an alkaline reaction, such as the sulphites. They form readily crystallisable salts, used in photography, and can be employed for producing pure catechol (Meister, Lucius and Brüning, D. R. P. 164666, 1904; Frdl. 1905–7, 129).

The mono- and di-ethyl ethers of catechol are prepared by heating under pressure a solution containing catechol, sodium hydroxide, and sodium ethyl sulphate or chloride in equivalent proportions. The ethers are then removed by steam distillation and separated by treatment with sodium hydroxide, in which only the monoether is soluble (J. Soc. Chem. Ind. 1896, 741; Eng. Pat. 16047, 1896). The diethers can be prepared by the action of alkalis on the monoethers (Frdl. 1894–7, 123; D. R. P. 92651).

Catechol monoethyl ether forms large clear colourless crystals, m.p. 26°–27°, b.p. 215°, which have an odour similar to that of thymol, and are soluble in alcohol and ether, but not in water.

The monoalkyl ethers of catechol, when fused or treated in solution with various proteids, albumoses, and peptones, yield compounds which are applied therapeutically (Fehrlin, D. R. P. 162656, 1906).

Monoethyl catechol ether *v.* GUAIACOL.

Dimethyl catechol ether *v.* VERATROL.

Catechol, when fused with aliphatic amines or heated with them in suitable solvents, yields stable amines which form useful photographic developers (D. R. P. 141101, 1903; Frdl. 1900–2, 1218). Other amino- and also nitro-derivatives are described by Meldola, Woolcott and Wray (Chem. Soc. Trans. 1896, 1332); Heinisch (Monatsh. 1894, 15, 229); Nietzki and Moll (Ber. 1893, 26, 2182); Blankswa (Rec. trav. chim. 1905, 24, 40); Grischkewitsch-Trochimowski (J. Russ. Phys. Chem. Soc. 1909, 41, 1324); Dakin (*l.c.*).

Good stable black, greenish, and bluish-black dyes, soluble in carbonates and alkaline sulphides, have been obtained by the action of aliphatic amines on catechol at 180°–222° (D. R. P. 84632; Frdl. 1894–7, 1048).

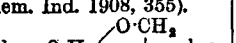
Methylene catechol ether $CH_2\langle{}^{O}_{O}\rangle C_6H_4$ is a colourless liquid; b.p. 172°–173° (Moureu, Bull. Soc. chim. 1897, 15, 654; Mameli, Atti. R. Accad. Lincei, 1906, (v.) 15, ii. 101; Perkin, Robinson, and Thomas, Chem. Soc. Trans. 1909, 1977). A number of derivatives have been prepared (Moureu, *l.c.* 1898, 19, 507;

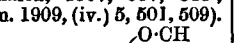
Medinger (Monatsh. 1906, 27, 237); Barger (Chem. Soc. Trans. 1908, 563, 2081); Barger and Ewins (*ibid.* 735).

Catechol diphenylmethylene ether

is prepared by gently heating catechol with benzophenone chloride; colourless prisms, m.p. 93° (Sachs and Thonet, Ber. 1904, 37, 3327.

The methylene ethers of catechol derivatives can be converted into chlorine derivatives of their cyclic carbonates by being heated with thionyl chloride (Wellcome and Barger, Eng. Pat. 15987, 1907; J. Soc. Chem. Ind. 1908, 355).

Catechol ethylenic ether  b.p. 216° (110°–111°, 31 mm.), is readily obtained by heating catechol with potash, ethylenic bromide and water in an atmosphere of hydrogen. Potassium permanganate, hydrogen iodide, and ammonia have no action on it, but it is oxidised by chromic acid to oxalic and carbonic acids. It yields a number of substitution derivatives (Moureu, Compt. rend. 1898, 126, 1426; Bull. Soc. chim. 1898, (iii.) 19, 507; Gattermann, Annalen, 1907, 357, 313; Lazennec, Bull. Soc. chim. 1909, (iv.) 5, 501, 509).

Catechol acetylenic ether  is prepared by dehydrating orthohydroxyphenoxyaldehyde with phosphoric anhydride in presence of quinoline. It is a colourless oil, boiling at 193°, and, when strongly cooled, forms brilliant white crystals, m.p. 16°–20°. It forms a dibromide $C_6H_4O_2(CH)_2Br_2$, m.p. 103°–104·5°, which, in contact with hot water, is converted into catechol, glyoxal, and hydrogen bromide (Moureu, Compt. rend. 1899, 128, 559).

Catechol forms a number of *acetals* (Moureu, Compt. rend. 1898, 126, 1656); also a vinyl derivative (Kurz Krause, Ber. 1897, 30, 1617; Pauly and Neukam, *ibid.* 1908, 41, 4151).

Catechol sulphonic acid $C_6H_3(OH)_2SO_3H$ is conveniently prepared by stirring together a meta-halogen phenol sulphonic acid with about an equal weight of sodium hydroxide in aqueous solution, and heating the mass to 250° for 8–10 hours. The mass is now dissolved in water and neutralised with a mineral acid such as sulphuric. The solution is evaporated and the sodium sulphate filtered off, whilst the concentrate solution of catechol sulphonic acid yields pure catechol when heated with mineral acids (Frdl. 1897–1900, 150; 1902–4, 100; D. R. P. 9623; Ellis, Eng. Pat. 14931, 1896).

Catechol disulphonic acid is obtained by treating catechol with 5 times the amount of fuming sulphuric acid (Cousin, Compt. rend. 1893, 117, 113), or by fusing phenol trisulphonic acid or its salts with alkalis and decomposing the alkali sulphonate so obtained with dilute sulphuric acid (Frdl. 1894–7, 118).

Halogen derivatives (Jackson and Boswell, Amer. Chem. J. 1906, 35, 519; Dakin, *l.c.*).

Monochlorcatechol $C_6H_3(OH)_2Cl$, m.p. 80°–81°, is obtained by the interaction of sulphuryl chloride with catechol in ethereal solution; by using a larger proportion of sulphuryl chloride, the *dichlocatechol*, m.p. 105°–106°, is obtained (Paratoner, Gazz. chim. ital. 1898, 28, i. 197).

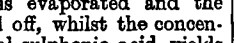
Trichlorcatechol $C_6H_3Cl_2O_2$ is obtained by the action of a chlorine solution in acetic acid or an acetic chloroform solution on catechol. It forms colourless odourless prisms, m.p. 104°–105°, with a burning taste. Excess of chlorine yields *tetrachlorocatechol* (Cousin, Compt. rend. 1895, 120, 840). The corresponding bromo-derivatives are obtained similarly (Cousin, *l.c.*).

The bismuth brominated catechols are recommended as a satisfactory substitute for tribromphenoxide, which is employed medically, under the name of 'xeroform.' They are produced by adding an acid solution of bismuth nitrate to alkaline, tetra-, tri-, or di-bromocatechol, or by introducing precipitated bismuth hydroxide into an alcoholic solution of the bromocatechol (D. R. P. 207544, 1909).

Catechol carboxylic acid

$$C_6H_4(OH)\cdot O\cdot CO_2H,\tfrac{1}{2}H_2O;$$

m.p. 240°, is formed by the action of ammonium carbonate on catechol at 130°–140° under pressure, or by heating catechol with glycerol and potassium hydrogen carbonate at 180°–210° in an atmosphere of carbon dioxide (Praxmarer, Monatsh. 1906, 27, 1199) The *di-carboxylic acid* can also be prepared. Derivatives of catechol carboxylic acid, used in medicine, are obtained by the interaction of alcohols and also of primary and secondary bases with catechol carbonate; thus:



$$=C_6H_4(OH)O\cdot CO_2C_2H_5$$

or by using aniline, the compound $C_6H_4(OH)O\cdot CONHC_6H_5$ is obtained, whilst with ethylene diamine it forms dicatechol-dicarbethylenediamide, $C_2H_4(NH\cdot CO_2C_6H_4\cdot OH)_2$ (Einhorn and Lindenberg, Annalen, 1898, 300, 135; D. R. P. 92535; Frdl. 1894–7, 1110). A number of similar compounds are described by Einhorn and Lindenberg (*l.c.*); Einhorn and Pfeiffer (Annalen, 1898, 310, 218).

Methyl catechol dicarbonate, m.p. 41°, is described by Syniewski (Ber. 1895, 28, 1874).

Carbonyl esters of catechol of the type $CO(OC_6H_4OR)_2$, also used in medicine, are prepared by the action of phosgene on the corresponding alkyl catechol in sodium hydroxide solution (D. R. P. 72806; Frdl. 1890–4, 854).

Catechol monoacetic acid

$$C_6H_4(OH)O\cdot CH_2\cdot CO_2H;$$

m.p. 131°, is obtained by the action of monochloracetic acid on catechol in aqueous or alkaline solution. When heated to 120°, it forms the *anhydride* , m.p. 56° (J. Soc. Chem. Ind. 1896, 588), which, when treated with water, yields the acid in a very pure state (D. R. PP. 87336, 87668, 87669, 89593; Frdl. 1894–7, 1106, 1107, 1108). The sodium salt of this acid is said to be a better remedy for phthisis and loss of appetite than guaiacol or its carbonate (Frdl. 1894–7, 1106). A large number of derivatives formed by the acid are described by Ludwig (J. pr. Chem. 1900, ii. 61, 345). *Catechol diacetates* are described by Drezgowski (J. Russ. Phys. Chem. Soc. 25, 157), and by Voswinckel (Ber. 1909, 42, 4561).

Catechol reacts with chloracetyl chloride or chloracetic acid, forming *chloroacetyl catechol*, thus:

$C_6H_4(OH)_2+ClCH_2{\cdot}COCl=C_6H_3(OH)_2CO{\cdot}CH_2Cl$

which, with ammonia or a primary aliphatic amine, yields amino-acetyl compounds of the type $RNHCH_2CO{\cdot}C_6H_3(OH)_2$, and these keto-compounds can be readily reduced to the corresponding alcohol (Imray, Eng. Pat. 26480, 1903; J. Soc. Chem. Ind. 1904, 1043; D. R. P. 13209; Frdl. 1890–4, 857) (*see* also ADRENALINE).

Aniline and chloroacetyl catechol form an *anilide* $C_6H_3(OH)_2CO{\cdot}CH_2{\cdot}NHPh$, which, with nitrous acid, yields *catecholglycophenyl triazine* $[C_6H_3(OH)_2]_2CO{\cdot}CH_2{\cdot}N{\cdot}Ph{\cdot}N:NCH_2CO$; m.p. 115°, with decomposition. The corresponding *tolyl*- derivative melts at 120°, and is prepared in a similar manner (Dzierzgowsky, Ber. 1894, 27, 1983; D. R. P. 71312 Frdl. 1890–4, 857).

Acetocatechol $C_6H_3Ac.(OH)_2$, m.p. 116°; *dimethoxyacetcatechol* $C_6H_3Ac.(OMe)_2$, and *catecholglycothiocyanate* $C_6H_3(OH)_2CO{\cdot}CH_2{\cdot}SCN$, m.p. 147°–150° have been prepared by Dzierzgowsky (*l.c.*). According to Abderhalden and Kautsch, the chloracetyl derivatives of catechol, when treated with ammonia, are resolved into their components (Chem. Zentr. 1910, ii. 1356).

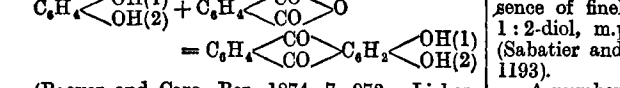
Alkyl acetyl catechol alkyl ethers, used in pharmacy, are obtained by the action of the alkyl acetyl chlorides on catechol monoalkyl ethers (J. Soc. Chem. Ind. 1906, 653; Eng. Pat. 25571, 1905; U. S. Pat. 822339, 1906).

A soluble tasteless product, $C_{10}H_8N_2O_6$, useful for medical purposes and as a substance from which other valuable technical products can be obtained, is formed by the condensation of catechol with alloxan in the presence of zinc chloride or mineral acids. It forms prismatic crystals, which decompose above 200° (D. R. P. 107720; Frdl. 1897–1900, 864).

Catecholdiantipyrine is obtained by mixing aqueous solutions of its constituents, and forms colourless needles; m.p. 78°–79° (Patein and Dufan, Compt. rend. 1895, 121, 532.

Piperidine catechol $C_5H_{11}N,[C_6H_4(OH)_2]_2$ forms white crystals which rapidly become red and then brown on exposure to air. It melts at 80°–81° (Rosenheim and Schidrowitz, Chem. Soc. Trans. 1898, 140).

Catechol, when treated with phthalic anhydride and sulphuric acid at 150°, yields alizarin; thus:

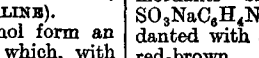


(Baeyer and Caro, Ber. 1874, 7, 972; Liebermann and Hohenemser, *ibid.* 1902, 35, 1778) (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

Catecholphthaleïn, $C_{20}H_{14}O_6$ is prepared by heating phthalic anhydride (3 parts) with catechol (2 parts) and zinc chloride (3 parts) to 140°–150° for 3–4 hours. The aqueous extract of the product is boiled with animal charcoal, and the filtrate, on cooling, deposits yellowish-white leaf crystals of the substance which sinters 80°–90°, but does not melt (Meyer and Pfotenhauer, Ber. 1907, 40, 1442; Bayer, Chem. Zentr. 1910, ii. 1524).

Under certain conditions, catechol combines energetically with diazo- compounds yielding azo-dyes (Witt and Mayer, Ber. 1893, 26, 1072; Orton and Everatt, Chem. Soc. Trans. 1908, 1021). Thus *Benzeneazocatechol* $C_6H_3(OH)_2N_2C_6H_5$, m.p. 165°, which dyes cotton mordanted with alumina a golden yellow, is formed by the interaction of an alcoholic solution of catechol and a concentrated solution of diazobenzene chloride, the mixture then being poured on to ice. The *nitro*- derivative $NO_2{\cdot}C_6H_4N_2C_6H_3(OH)_2$ colours alumina mordants red, and iron and chromium mordants brown; the sodium sulphonate $SO_3NaC_6H_4N_2C_6H_3(OH)_2$ colours wool mordanted with alumina, yellow; with chromium, red-brown. Similar toluene compounds have also been obtained. Catechol also forms triazo- or azoimido- compounds (Rupe and Majewski, Ber. 1900, 33, 3401).

Catechol glycoisoquinoline



forms glittering orange-coloured crystals which give a red colouration with very dilute ferric chloride and a green colour in presence of excess of the latter; both the base and the chloride dye cotton mordanted with iron, aluminium, or chromium salts, black-yellow or reddish-brown respectively (Nencki, Ber. 1894, 27, 1969).

Catecholglycotetrahydroquinoline $C_{17}H_{17}NO_3$ crystallises in yellow lustrous plates; m.p. 170° (Nencki, *l.c.*).

Catechol, when heated with zinc chloride and formic acid, yields *aurin* dyes which give fast colours with metallic oxide mordants (Caro, Ber. 1893, 26, 254).

Catechol tannins are employed in colouring leathers (J. Soc. Chem. Ind. 1907, 423, 882; *ibid.* 1909, 1151).

A number of products obtained by the condensation of catechol with ketones are described by Fabinyi and Széky (Ber. 1905, 38, 2307).

Catechol, when warmed with an alcoholic solution of picryl chloride containing sodium, yields 3 : 5-*dinitro-o-diphenylene oxide*, $C_6H_4O_2{\cdot}C_6H_2(NO_2)_2$, m.p. 192°–192·5° (Hillyer, Amer. Chem. J. 1900, 23, 125).

Catechol heated with hippuryl chloride on the water-bath yields *o-hydroxyphenyl hippurate* $NHBz{\cdot}CH_2{\cdot}CO_2C_6H_4{\cdot}OH$, m.p. 134°–136°, which with hydrogen chloride gives the anhydride $C_{15}H_{11}O_3N$, m.p. 232°–233° (Fischer, Ber. 1905, 38, 2926).

When catechol is hydrogenated in the presence of finely divided nickel, cis-cyclohexane 1 : 2-diol, m.p. 75°–76°, b.p. 225°, is formed (Sabatier and Mailhe, Compt. rend. 1908, 146, 1193).

A number of quinone and halogen quinone derivatives of catechol are described by Jackson and Koch (Amer. Chem. J. 1901, 26, 10); Jackson and Porter (*ibid.* 1903, 30, 518); Jackson and Russe (*ibid.* 1906, 35, 154; Ber. 1905, 38, 419). Other derivatives of catechol have also been prepared (Cousin, Ann. Chim. Phys. 1898, (vii.) 480; 1899, (vii.) 18, 76; Bischoff, Ber. 1900, 33, 1669; Wisinger, Monatsh. 1900, 21, 1007; Bischoff and Hedenström, Ber. 1902, 35, 3452; Bischoff and Fröhlich, Ber. 1907, 40, 2779, 2790; Barger and Ewins, Chem. Soc. Trans. 1909, 552, 1482; Fourneau, J. Pharm. Chim. 1910, (vii.) 1, 55, 97).

Catechol phosphines and chlorophosphines

(Krauer, Ber. 1894, 27, 2565); phosphites and sulphites (Auschütz and Posth, Ber. 1894, 27, 2751); also a number of antimonyl catechol compounds (Causse, *l.c.*), some bismuth derivatives (Richard, Chem. Zentr. 1900, ii. 629), and a lead salt (Jackson and Koch, Ber. 1898, 31, 1458), have been prepared.

Homologues of catechol, such as homocatechol (*o*-dihydroxytoluene), can be prepared by heating the corresponding alcohol with catechol in the presence of zinc chloride in open or sealed vessels (Merck, Frdl. 1894–7, 115; D. R. P. 78882), or by the interaction of persulphates and *p*-phenol derivatives in alkaline solution, the product then being warmed with acid (Frdl. 1894–7, 121; D. R. P. 81298).

$$C_6H_4\begin{matrix}OH(1)\\R\ (4)\end{matrix} + K_2S_2O_8 + KOH$$
$$= C_6H_3\begin{matrix}OK(1)\\OSO_2OK(2)\\R(4)\end{matrix} + K_2SO_4 + H_2O$$
$$C_6H_3\begin{matrix}OK(1)\\OSO_2OK(2)\\R(4)\end{matrix} + H_2SO_4 + H_2O$$
$$= C_6H_3\begin{matrix}OH(1)\\OH(2)\\R(4)\end{matrix} + 3KHSO_4$$

This method can be applied to the production of a large number of various derivatives.

CATECHU or CUTCH. There are several varieties of catechu or cutch bearing different names according to the country or plants from which they are obtained. The following are those principally employed by dyers and tanners: Gambier catechu, Bengal or Acacia catechu, Bombay or Areca catechu, and Mangrove cutch.

Although catechu has perhaps received greater attention than other natural dyes, the results have been so varied that the chemistry of the subject was until recently in a most unsatisfactory condition. Some confusion has arisen from the non-appreciation of the fact that the main constituents of Gambier and Acacia catechu are not identical, and some uncertainty has also apparently existed as to the botanical origin of the commercial varieties. Bombay catechu is, for instance, occasionally referred to as originating from the *Acacia catechu*, and *Bengal catechu* from the *Areca catechu* (Linn.); and in many cases, at the present time, it is impossible to ascertain the botanical derivation of commercial brown cutch preparations.

Gambier catechu.—Gambier, yellow cutch, cubical cutch, cube gambier, or terra japonica, is obtained from the *Uncaria gambier*, an extensive scandent bush which is met with, both wild and cultivated, in Malacca, Penang, and Singapore. The catechu is isolated by extracting the leaves and twigs with hot water until the liquid becomes syrupy, the insoluble matter being removed from time to time by means of a strainer. On cooling, the pasty mass is cut into cubes with sides 1 inch in length and dried on bamboo trays.

Catechin $C_{15}H_{14}O_6,4H_2O$, the crystalline principle, was first described by Nees van Esenbeck (Annalen, 1832, 1, 243), was subsequently examined by Berzelius in 1837 (J. 14, 235), and more recently by numerous chemists. To isolate catechin, Löwe (Zeitsch. anal. Chem. 13, 113) devised the following method: catechu is washed with cold water to remove catechutannic acid, well pressed, allowed to dry, and dissolved in hot acetic ester. The filtered solution is evaporated and the residue crystallised from hot water.

According to Perkin and Yoshitake (Chem. Soc. Trans. 1902, 81, 1162), a combination of this method and that of Berzelius (*l.c.*) gives good results.

The finely powdered catechu is extracted with 10 times its weight of boiling ethyl acetate, the solution is evaporated, and the residue crystallised from 10 times its weight of water. The product is again dissolved in boiling water, and lead acetate solution added, drop by drop, until a coloured precipitate is no longer formed, and the filtrate is almost colourless; the latter, while hot, is treated with sulphuretted hydrogen, the lead sulphide removed, and the crystals, which separate on cooling, are collected, washed, and allowed to dry at the ordinary temperature. The substance is now practically colourless, and the yield greater than if the purification had been effected by frequent crystallisation from water.

The formulæ which have been assigned to catechin are very numerous, and it has only recently been shown by Kostanecki and Tambor (Ber. 1902, 35, 1867), and simultaneously by Perkin and Yoshitake (*l.c.*), that it is correctly represented as $C_{15}H_{14}O_6,4H_2O$.

Catechin forms colourless needles, and when crystallised from water the air-dry product melts at 96° (Clauser, Ber. 1903, 36, 101). After standing over sulphuric acid, it possesses the formula $C_{15}H_{14}O_6,H_2O$, and melts at 176°–177°, and this is also the melting-point of the anhydrous substance. Catechin is readily soluble in boiling water and cold alcohol, and gives with lead acetate solution a colourless precipitate, and with ferric chloride a deep-green liquid. With pine wood and hydrochloric acid, it gives the phloroglucinol reaction.

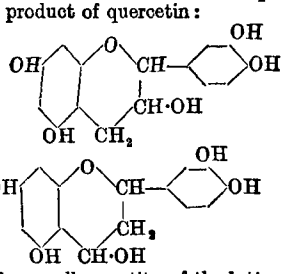
On fusion with alkali, *protocatechuic acid*, *phloroglucinol*, and probably acetic acid are produced, and it is interesting to note that catechu has been considerably employed for the commercial preparation of the former compound.

Schutzenberger and Rack (Bull. Soc. chim. 4, 6) have described a dibenzoylcatechin; and Liebermann and Tauchert (Ber. 1880, 13, 695), diacetyl catechin, diacetyl dichlorcatechin, and diacetyl dibromcatechin; but their formulæ for these compounds are now known to be incorrect.

Penta-acetyl catechin $C_{15}H_9O_6(C_2H_3O)_5$; colourless needles, m.p. 124°–125° (Kostanecki and Tambor); *pentabenzoyl catechin*, $C_{15}H_9O_6(C_7H_5O)_5$, colourless needles, m.p. 151°–153°; *tetrabenzoyl catechin*, $C_{15}H_{10}O_6(C_7H_5O)_4$; prisms, m.p. 171°–172° (Perkin and Yoshitake); *disazobenzene catechin*, $C_{15}H_{12}O_6(C_6H_5N_2)_2$, salmon-red needles, m.p. 193°–195° (Etti, P. and Y.); *acetyldisazobenzene catechin*, orange-red needles, m.p. 253°–255° (P. and Y.); *catechin tetramethylether* $C_{15}H_{10}O_2(OCH_3)_4$, needles, m.p. 144°–146° (K. and T.); *acetyl catechin tetramethylether* $C_{15}H_9O_2(OCH_3)_4C_2H_3O$, needles, m.p. 92°–93°; and *catechin pentamethylether* $C_{15}H_9O(OCH_3)_5$ (K. and T.), have been prepared.

When catechin tetramethylether, suspended in water, is oxidised with potassium permanganate, it gives *veratric acid*, and most probably

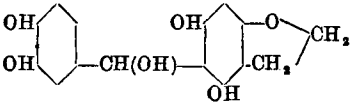
phloroglucinol dimethylether (Trans. Chem. Soc. 1905, 87). As the result of this investigation, Perkin considered that catechin was possibly a reduction product of quercetin:



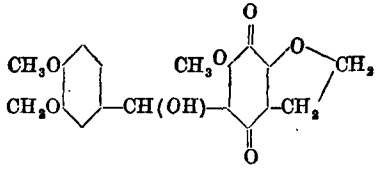
or

and indeed a small quantity of the latter colouring matter is present in catechu (Löwe; Perkin, *ibid.* 71, 1135).

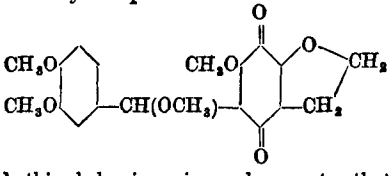
More recently, Kostanecki and Lampe (Ber. 1906, 39, 4007) have shown that when catechin tetramethylether is brominated in the presence of sunlight, only a *monobromcatechin tetramethylether*, m.p. 173°–174°, is produced, whereas the above constitutional formulæ require the formation of a dibromo- compound. When oxidised with permanganate, bromcatechin tetramethylether gives veratric acid, so that the bromine must have replaced one hydrogen of the phloroglucinol nucleus. Kostanecki and Lampe have assigned the following constitution to catechin:—



and this is in harmony with many of the properties of this substance. When catechin tetramethylether is oxidised with chromic acid, *catechone trimethylether*, orange-yellow needles, m.p. 210°, is produced (K. and T.):

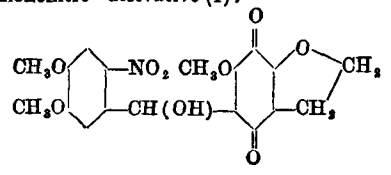


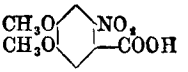
whereas catechin pentamethylether gives the tetramethyl compound:



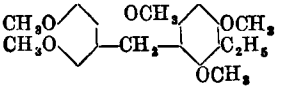
and this behaviour is analogous to that of leucomaclurin pentamethylether (*see* OLD FUSTIC).

When catechone trimethylether is nitrated, a mononitro- derivative (1):

(1) 

(2) 

m.p. 141°, is obtained, and on oxidation yields nitroveratric acid (2). Finally, by the reduction of catechin tetramethylether with sodium and alcohol, an oil is produced which, on treatment with methyl sulphate, gives *pentamethoxyethyldiphenylmethane*



a reaction which points clearly to the presence of the cumaran ring in catechin.

Catechin is oxidised in aqueous solution by potassium ferricyanide in the presence of potassium acetate with formation of an orange-coloured amorphous compound (Perkin), which dyes mordanted calico orange-brown shades which are fairly fast to soap. It is probable that this dyestuff is related to the catechone of Kostanecki and Tambor, and which was obtained by these authors in the form of its tri- and tetramethyl ethers.

Catechutannic acid. In addition to catechin, gambier catechu contains a small amount of catechutannic acid, and this substance is present in considerable quantity in the browner varieties of cutch. To isolate it, the following method has been employed:—

A hot aqueous extract of catechu is allowed to stand until no more catechin is deposited, and the clear liquid is evaporated to dryness. The residue is dissolved in alcohol, the solution treated with ether to precipitate impurities and then evaporated to dryness.

Catechutannic acid consists of an amorphous reddish-brown powder, readily soluble in water and alcohol, insoluble in ether. According to Löwe (Fr. 13, 121), it possesses the formula $C_{21}H_{18}O_8$, and gives a lead salt $3PbO,2C_{21}H_{18}O_8$, but this most probably requires revision.

According to Etti (Annalen, 186, 332), catechutannic acid is an anhydride of catechin, and is apparently derived from this substance by elimination of water. It is said to be produced when an aqueous solution of catechin is heated to 110° (Löwe, *ibid.* 12, 285), or by boiling catechin with solutions of the alkali carbonates. Again, catechin is decomposed at its melting-point with evolution of water and formation of a product resembling catechutannic acid, and aqueous solutions of catechin on long standing become brown-coloured with apparent formation of this compound. That the products obtained by these methods resemble catechutannic acid is certain, but the subject has not been fully investigated.

Catechutannic acid solution gives a precipitate with lead acetate, and also resembles that of catechin in giving a green colouration with ferric chloride, and the phloroglucinol reaction with pinewood and hydrochloric acid. It is a powerful tanning agent, and appears to differ but little from the so-called 'catechol' tannins.

Three other catechin anhydrides have been described, viz. the *second* anhydride $C_{42}H_{34}O_{15}$ (?) (Etti), which is produced by heating catechutannin to 162°; the *third* anhydride $C_{21}H_{16}O_7$ (?) formed by digesting catechin with boiling dilute sulphuric acid for several hours; and the *fourth*

anhydride, which is obtained by heating catechin with hydrochloric acid at 160°–180°. These compounds consist of reddish-brown powders, and the fourth substance is insoluble, both in alkaline solutions and all solvents. A product similar in properties to Etti's fourth anhydride, is readily formed by adding sulphuric acid to an acetic acid solution of catechin (Perkin). A bright orange powder almost immediately separates, and this, on analysis, gave C=63·26 p.c.; H=3·89 p.c. It is interesting to note that the formation of these red anhydrides, or *phlobophanes*, is characteristic of all the catechol tannins.

According to Perkin and Yoshitake, gambier catechu contains a small quantity of a second catechin, which crystallises in small prisms, devoid of water of crystallisation, and melts at 235°–237°. Its general reactions are identical with those of ordinary catechin, and by fusion with alkali it also gives *phloroglucinol* and *protocatechuic* acid. The azobenzene compound $C_{15}H_{12}O_6(C_6H_5N_2)_2$, orange-red needles, melts at 215°–217°.

Finally, there are present in catechu, certain brown substances known as *rubinic* and *japonic* acids, which, according to some writers, appear to have been formed by the oxidation of the catechin. Their chemical nature is, however, unknown.

Catechin, though largely employed for tanning purposes, does not precipitate a gelatine solution, and is not itself a tannin matter. On the other hand, it is absorbed by the hide, and there gradually passes into catechutannic acid.

Dyeing Properties.—On cotton, catechu is largely used for the production of the well-known 'catechu brown,' which is exceedingly fast to light, acid and alkaline solutions, and also to bleaching powder. To obtain this, cotton is steeped in a hot solution of catechu (1–2 p.c.) to which has been added about 6 p.c. of copper sulphate, reckoned on the weight of the catechu employed. The material is allowed to remain in the bath as it cools, and without washing is then treated in a warm or boiling bath containing 1 or 2 grams of bichromate of potash per litre. According to Hummel and Brown (J. Soc. Chem. Ind. 1896, 15, 422), in this operation the copper sulphate probably converts the catechin into catechutannic acid, and this is subsequently oxidised to japonic acid by the action of the bichromate. The colour is apparently intensified by the formation of a basic copper chromate. Gambier catechu is also employed in dyeing compound shades with logwood fustic and alizarine in conjunction with bichrome, and with bismarck brown, magenta, &c. In the latter case catechu-tannin forms the mordant for the basic colour.

Wool may be dyed with catechu in a similar manner to cotton. In silk-dyeing, catechu is largely used for weighting purposes. The silk is steeped in basic ferrous sulphate solution, then in potassium ferrocyanide and hydrochloric acid, which causes the production of prussian blue on the fibre. It is then worked in a strong solution of gambier to which stannous chloride solution has been added.

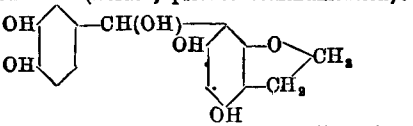
Bengal or Acacia catechu.—Bengal catechu is derived from the *Acacia catechu*, a tree 15 to 20 feet high, which is common in most parts of India and Burma. To isolate the catechu which is present in the red heartwood, the tree is cut down while it is fullest of sap, and the internal portion is sawn into small sticks and extracted with boiling water. The liquid thus obtained is concentrated over a fire, and then allowed to evaporate spontaneously in shallow dishes. The extract thus obtained comes into the market as *Pegu* catechu, Brown cutch, and Brown catechu (Crookes, Dyeing and Calico Printing).

A purer substance, *kath*, or the pale catechu of India, is prepared by suspending twigs in the hot concentrated extract and collecting the crystals which thus separate.

Acacatechin $C_{15}H_{14}O_6,3H_2O$ can be obtained from the acacia kath by methods identical with those which are employed for the isolation of catechin from gambier catechu. It melts at 204°–205°, is somewhat more sparingly soluble in water than catechin, and when fused with alkali gives *phloroglucinol* and *protocatechuic acid*. The reactions of acacatechin and catechin, in so far as they have been observed, are identical, and there is no difference in the composition of their derivatives when prepared under similar conditions. On the other hand, the melting-points of the substances themselves, and also of their derivatives, differ widely, as is evident from the following table (Perkin and Yoshitake):—

	Acacatechin	Catechin
Pentaacetyl derivative	158°–160°	124°–125°
Pentabenzoyl ,,	181°–183°	151°–153°
Azobenzene ,,	198°–200°	193°–195°
Tetramethyl ,,	152°–154°	144°–146°
Acetyl ,,	135°–137°	92°–93°

It appears certain, therefore, that catechin and acacatechin are isomerides, and it is possible that the latter may, on the basis of Kostanecki and Lampe's formula for catechin be represented thus (Perkin, private communication):



a point which should not be difficult to determine.

Bombay or Areca catechu. This variety is obtained from the fruit of the *Areca catechu*, or betel-nut palm, a tree which is common in tropical Asia. Though its chief constituent resembles catechutannic acid, catechin itself has not been isolated from this product. It possesses a bright-chocolate and sometimes an orange-brown colour, and yields, on dyeing, very similar results to the ordinary cutches.

Mangrove cutch. Mangrove cutch is obtained from the bark of the mangrove *Ceriops candolleana*, and is of somewhat recent employment. In its preparation it is preferable to extract the fresh bark, which is of a light colour internally, rather than the stored product which has become red, or is said to have sweated. The extract, on evaporation, becomes deep-red in colour, and the object of the manufacturer is to prevent this anhydride formation from going too far, otherwise a certain portion of the extract is rendered insoluble in water.

By fusion with alkali, it gives *protocatechuic acid*, but at present no catechin has been isolated from it (Perkin, private communication). When dissolved in sodium bicarbonate solution, acetic

ester extracts an almost colourless tannin, which possesses the properties of a catechol tannin.

For many purposes, Mangrove cutch is competing closely with the other varieties of catechu, and this competition will no doubt become keener if its quality can be further improved.

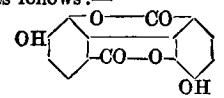
Mahogany. According to Caseneuve (Ber. 8, 828), mahogany wood contains a catechin.

Kino or **Gum kino** (*see* under KINOS).

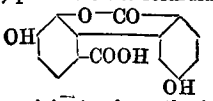
A. G. P.

CATELLAGIC ACID $C_{14}H_8O_6$. Schiff (Ber. 12, 2590), on heating protocatechuic acid with arsenic acid, obtained a substance which he named catellagic acid, and to this he assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. Perkin and Nierenstein (Chem. Soc. Trans. 87, 1417) obtained apparently the same substance by the oxidation of protocatechuic acid, and also parahydroxybenzoic acid with potassium persulphate and sulphuric acid. According to the latter authors, catellagic acid crystallises from pyridine in colourless needles, which melt above 360°, and sublime with but moderate carbonisation at higher temperatures. Solutions of the alkali hydroxides dissolve it with a pale-yellow colour, and with nitric acid it gives a magenta-coloured liquid. *Diacetylcatellagic acid*, colourless prismatic needles, melts at 322°-324°.

Catellagic acid, by distillation with zinc-dust, gives *fluorene*, and is closely related to ellagic acid. Its constitution (P. and N.) may be expressed as follows:—



From the oxidation products of parahydroxybenzoic acid, Perkin and Nierenstein isolated, in addition to catellagic acid, a second compound, $C_{14}H_8O_6$, colourless needles, m.p. above 360°. This, which gives the diacetyl derivative, $C_{14}H_6O_6(C_2H_3O)_2$ colourless needles, m.p. 267°-268°, and by distillation with zinc-dust fluorene, possesses the formula:



and evidently originates from the interaction of one molecule of protocatechuic acid and one of parahydroxybenzoic acid. A. G. P.

CATHARTIC ACID *v.* SENNA LEAVES.

CATHARTIN *v.* SENNA LEAVES.

CATHARTOGENIC ACID *v.* SENNA LEAVES.

CATHARTOMANNITE *v.* SENNA LEAVES.

CAULIFLOWER. A variety of *Brassica oleracea*, in which numerous imperfect flowers form a compact head, which forms the main edible portion.

An American analysis shows the edible portion to contain:

Water	Protein	Fat	Soluble carbohydrates	Ash
90·8	1·6	0·8	6·0	0·8

H. I.

CÂY CÂY FAT or **COCHIN CHINA WAX** *v.* WAXES.

CAYENNE PEPPER *v.* RESINS.

CEDAR CAMPHOR *v.* CAMPHORS.

CEDAR OIL *v.* OILS, ESSENTIAL.

CEDRA. (*Cedrat*, Fr.) The fruit of a species of orange, citron, or lemon. The peel is very thick, covered with an epidermis containing a fragrant essential oil, used for flavouring preserves, also used whole for wet comfits, and cut in quarters for dry comfits. A liqueur is made from it by gathering the fruit before it is ripe, and grating the peel into brandy.

CEDRIRET. A substance found in wood-tar by Reichenbach and recognised by Liebermann as a quinone-like substance and termed by him *cærulignone*. Hofmann showed that it was tetramethoxydiphenyl quinone, formed by the oxidation of pyrogallol dimethyl ether (*v.* CŒRULIGNONE and QUINONES).

CELERY. *Apium graveoleus.* The blanched stems are used for food.

The composition, as given by American analyses, is:

Water	Protein	Fat	Carbohydrates	Ash
94·4	1·4	0·1	3·0	1·1

A more detailed analysis is given by Church (Foods, 1889):

Water	Protein	Starch and mucilage	Sugar	Cellulose	Ash
93·3	1·4	1·6	2·0	0·9	0·8

Mannitol is one of the chief carbohydrate constituents. Asparagine (about 0·5 p.c.) and tyrosine, are among the nitrogenous constituents (Bamberger and Landsiedl, Monatsh. 1904, 25, 1030).

The characteristic odour and flavour of celery are due to an essential oil, which, according to Ciamician and Silber (Ber. 29, 1799; 1897, 30, 492, 1419), consists of a terpene, probably $C_{15}H_{24}$, and two acid bodies, *sedanonic* acid $CO_2H{\cdot}C_6H_8{\cdot}CO{\cdot}C_4H_9$ and *sedanolic acid*

$$CO_2H{\cdot}C_6H_8{\cdot}CH(OH){\cdot}C_4H_9$$

the anhydride $C_6H_8\langle \begin{matrix} C(:C_4H_8) \\ CO \end{matrix} \rangle O$ of the former and the lactone $C_6H_8\langle \begin{matrix} CH(C_4H_9) \\ CO \end{matrix} \rangle O$ of the latter appear to be the constituents upon which the smell of the celery depend. Palmitic acid and a phenolic substance are also present.

H. I.

CELERY OIL *v.* OILS, ESSENTIAL.

CELESTINE BLUE *v.* OXAZINE DYESTUFFS.

CELESTITE or **Celestine.** Native strontium sulphate ($SrSO_4$), forming orthorhombic crystals isomorphous with barytes ($BaSO_4$). The crystals are colourless or yellowish, but sometimes they show a pale tinge of sky-blue, and on this account the mineral receives its name. The mineral is often very like barytes in appearance and it is also heavy (sp.gr. 3·9; of barytes, 4·5); it is most readily distinguished by the colour it imparts to the Bunsen flame. Numerous finely crystallised specimens have been found in the red marls of Triassic age in the neighbourhood of Bristol, and in the sulphur-mines near Girgenti in Sicily. The largest crystals, measuring a foot across, are from a cave in limestone on Strontian Island, Lake Erie, Ohio. The mineral is dug in numerous shallow pits in Gloucestershire and Somersetshire, the production amounting to about 20,000 tons per annum, valued at about 1*l.* per ton. Most of this is exported to Germany, where, in the form of strontium hydroxide, it is used in the refining of beet-sugar. It is also converted into strontium nitrate for making red fire in pyrotechny.

L. J. S.

CELLOSE (CELLOBIOSE) *v.* CARBOHYDRATES.
CELLULASE *v.* ENZYMES.

CELLULOID is a colloid composed of soluble nitrocellulose, approaching $C_{12}H_{16}(NO_2)_4O_{10}$ in composition, together with camphor. It is obtained by gelatinating nitrocellulose by means of a solution of camphor in ethyl alcohol or a similar menstruum. The word 'celluloid' is a registered trade-mark in the United States. The substance was first produced by Daniel Spill, of Hackney, England, and came into commerce under the name of xylonite. Spill's method of converting the nitrocellulose has been followed for more than 40 years. Great improvements in the manufacture, especially in mechanical features, were made by John W. Hyatt, of Newark, N.J., U.S.A., and the United States quickly became the centre of the new industry. Here also originated improved methods and apparatus for the manufacture of the large quantities of pure nitrocellulose required; for the regeneration of the acid-baths; and the safe dehydration of the wet nitrocellulose.

The nitrocellulose employed is preferably made from tissue paper, in the form of shreds or strips, by subjecting it for 20 minutes to the action of a bath of mixed sulphuric and nitric acids containing 19–20 p.c. of water, at a temperature of 30° and upwards. The resulting nitrocellulose is thoroughly washed with water to free it from acid, and bleached with hypochlorite solution if necessary. After treatment in a centrifugal machine, it is pressed between absorbent pads to remove nearly all of the remaining water; or better, the water is replaced by alcohol, ordinary drying having been abandoned on account of the danger of explosion. If the alcohol replacement process is employed, care is taken to leave exactly the quantity of alcohol in the material necessary for its subsequent conversion.

To 100 parts of pyroxylin (containing 40 of alcohol), 35 of camphor, and the necessary pigments and fillers, are added and thoroughly incorporated in a kneading machine. Transparent material receives a small percentage of urea, dissolved in methyl or ethyl alcohol, as a stabilizer. The dough-like mass is worked and formed into sheets between slightly heated rolls. These sheets are consolidated in hydraulic presses, heated to about 75° into a solid cake, 125 or 90 cm. long and 50 cm. wide, from which, after cooling, sheets of the desired thickness are cut. Or the mass taken from the rolls is placed in a heated cylindrical hydraulic press, provided with suitable nozzles and dies, from which it emerges in the shape of tubes, rods, or the like, of any desired cross-section. Rods may also be made out of the cakes previously mentioned by forcing a cutting tool through them. All this material has to be freed from its excess of solvent, and is seasoned in fire-proof rooms heated to 30°, where it is kept for a period of one to six weeks, or even longer, according to thickness. The camphor solvent usually employed is denatured alcohol, owing to the fiscal policy of the countries concerned; but wood alcohol, pure grain alcohol, and a mixture of one or both of these with fusel oil, or its various constituents have also been widely used. Owing to the great fluctuations in the price of camphor in recent years, the attempts to make this substance synthetically, and to find a substitute for it, have been pursued with vigour. Synthetic camphor in commercial quantities is an accomplished fact, and is the equivalent of the natural product. The search for substitutes was begun in the United States in the early eighties; the most suitable found so far being acid derivatives of aromatic amines. This work started a flood of patents in European countries, especially Germany, most of them unimportant.

Celluloid is coloured by means of mineral colours, lakes, and coal-tar dyes, the latter being chiefly used for transparent material. Owing to its plasticity, especially when still containing part of its volatile solvents, and the ease with which it is welded in this condition, it lends itself readily to the imitation of a great variety of natural products, and by various mechanical processes perfect imitations of ivory, tortoise-shell, amber, marble, agate, lapis-lazuli, malachite, &c., are made from masses of different colour and composition.

Celluloid, while rather inflammable, is non-explosive under any conditions to which it may be subjected in the work of cutting, turning, or moulding. Its specific gravity varies with its composition: it is 1·35 for the pure material, a value lower than that possessed by a simple mixture. Careful determinations of the heats of combustion of seasoned celluloid, and the nitrocellulose and camphor entering into its composition, do not warrant the assumption of a mechanical mixture; nor does the study of the behaviour of fine shavings heated in an evacuated container for a long period. Though boiling with solvents, such as chloroform, petroleum ether, and carbon disulphide, which have no gelatinating action on celluloid, extracts the camphor from the compound, such behaviour cannot be regarded as establishing a simple mixture in view of the foregoing observations. Celluloid turns plastic at a temperature of 75°, and in practice it is usually softened in boiling water or on a steam table preparatory to moulding. This property of turning plastic at a comparatively low temperature, and its hardness and elasticity at ordinary temperatures, as well as its resistance to the action of water, dilute acids, and many other agents, constitute its great technical value. It is used extensively in the manufacture of combs, brush and mirror-backs, knife-handles, piano-keys, toys, rims of eye-glasses, and a great variety of other articles. R. S.

CELLULOSE, considered physiologically, is the main product of vegetable life. It is the preponderating constituent of all vegetable tissues, and essential to the cell as the structural unit. For while the synthesising activity of the cell is identified with its protoplasmic contents, its main function is the building up of non-nitrogenous substances, of which cellulose is the chief; elaboration of cellulose, in fact, is synonymous with growth. As an organic product it is known to us in the specialised and diversified forms of plant structures, which are employed in industries either in their original form or after treatment for separation of their fibrous components.

Cellulose is the basis of our staple textile and paper-making industries, and when modified by various chemical treatments, it is the basis of

modern high explosives, 'celluloid' products and 'artificial silk.'

Cellulose, of course, is an incidental component of vegetable foodstuffs, and its significance in connection with agriculture and all that appertains to the cycle of processes organically interdependent of the animal and vegetable worlds, is paramount.

By cellulose, as a chemical individual, we understand usually the residue from the exhaustive alternate treatment of vegetable tissues with alkaline solvents and weak oxidants. Generally, no cellulose is isolated on the large scale except as the result of a chemical treatment, more or less drastic, of fibrous raw materials; and all that we know of cellulose as a chemical individual results from the study of products so obtained. The typical cellulose is the substance of bleached cotton, the bleaching process such as above described removing the substances other than cellulose with which it is associated in the plant. So obtained, it is a white substance, translucent when viewed under the microscope, but more or less opaque in the mass. This appearance is a consequence of the peculiar form of the cotton fibre, a flat thin-walled tube, the fibrillæ of which are membranously disposed.

The following brief outline of the special chemistry of cellulose necessarily precedes an account of its industrial applications, so far as they involve chemical principles or processes of treatment.

Cellulose.—Generally the non-nitrogenous skeleton of plant structures. Type: the fibre substance of cotton, freed from associated 'impurities' by processes of (1) alkaline hydrolysis and oxidation (bleaching); (2) digestion with hydrofluoric and hydrochloric acids, to remove mineral impurity or ash constituents.

Composition.—Elementary: C,44·4; H, 6·2; O,49·4; whence the empirical formula, $C_6H_{10}O_5$.

Constitution.—By solution in sulphuric acid as disulphuric ester $n\cdot[C_6H_8O_3(SO_4H)_2]$ and ultimate hydrolysis, the colloidal aggregate is resolved mainly to dextrose (Flechsig. Zeitsch. physiol. Chem. 7, 523). The identity

$$[n\cdot C_6N_{10}O_5]+n\cdot H_2O=n\cdot C_6H_{12}O_6]$$

which has been assumed, has not been verified experimentally; a maximum yield of 90–100 p.c. dextrose [theory, 111·11], accompanied by acid products, leaves the problem undetermined (Ost and Wilkening; Chem. Zeit. 34, 461). Cellulose is thus variously regarded:

1. As a polyhexose anhydride; (*a*) aldose; (A. G. Green, Zeitsch. Farb. Chem. 3, 97), (*b*) ketose (Fenton, Cross and Bevan, Chem. Soc. Trans. 82, 361, 366).

2. As a polycyclohexane derivative; this view is based on considerations of density and molecular volume (Cross and Bevan, Ber. 1909, 42, 2198.

3. As an essentially labile aggregate, that is of variable constitution or configuration, varying according to the action of reagents (Cross and Bevan, Chem. Soc. Trans. 85; Cellulose Researches, ii. 1905).

Cellulose and water.—Hydration. Constitutional water is retained by cellulose in the air-dry condition. Cotton holds 6–8 p.c., varying with temperature and moisture of atmosphere. Cotton which has been hydrated by treatment with alkalis (mercerisation) or solvents (*infra*) or by prolonged attrition in presence of water, shows an increased capacity for moisture when air-dry, and retains 9–11 p.c. Conversely, the action of condensing acids (HCl,HBr) produces modified aggregates ('hydrocellulose'), with a lower capacity (3–5 p.c.). Cellulose separated from its solutions, or regenerated from its derivatives by the action of reagents, shows a maximum hydration capacity; the colloidal or gelatinous hydrates having the composition (in contact with water at ordinary temperatures):

Cellulose . . .	20–10 p.c.
Water . . .	80–90 „

Cellulose and solvents.—Insoluble in all neutral solvent liquids, cellulose is dissolved by:

1. Concentrated solutions of zinc chloride (40–50 p.c. $ZnCl_2$), on heating at 80°–100°; when previously hydrated, at lower temperatures;

2. Solution of zinc chloride in twice its weight of HCl·Aq. (35 p.c. HCl): this reagent rapidly attacks and resolves the aggregate;

3. Solutions of cuprammonium hydrate containing:

Cu, as $CuO\cdot nH_2O$ . . .	2·5–3·5 p.c.
NH_3 (as NH_4OH) . . .	15 p.c.

From solutions 1 and 3, the cellulose may be recovered quantitatively, but as a hydrate and otherwise modified in constitution.

Reactions.—The above reactions resulting in solution of the cellulose are characteristic; otherwise it is exceptionally non-reactive. By dilute solutions of iodine, in presence of certain dehydrating agents, it is coloured blue.

A. Cellulose compounds, *i.e.* synthetical derivatives. Esters.

(*a*) **Nitrates.** By direct reaction with nitric acid, usually in presence of sulphuric acid, in which case unstable mixed esters are formed as a stage in the reaction, the NO_3 displacing the SO_4H residues. The esters are formed without sensible structural modification. They are purified from residual SO_4H by prolonged boiling with water, and are then 'stable.' A series of these esters is known, the highest approximating to the trinitrate (C_6) (gun-cotton); the intermediate terms—dinitrate—being soluble in ether-alcohol (collodion cotton), the lowest having physical properties but little different from the original cellulose.

These esters are variously formulated as nitrates of a reactive unit of $C_6-C_{12}-C_{24}$ dimensions.

Solvents.—The special solvents of these esters are acetone, ether-alcohol, nitrobenzene.

Saponification.—By certain alkaline and reducing agents (alkaline sulphydrates) the nitric groups are eliminated and cellulose regenerated.

(*b*) **Acetates.** By reaction with acetic anhydride under various conditions: (1) at 110°: direct formation of monoacetate (C_6) insoluble in all neutral solvents and in the solvents of cellulose. (2) At 140°–160°: formation of higher acetates, attended by solution in the reaction mixture. (3) In presence of catalytic agents ($ZnCl_2-H_2SO_4-H_3PO_4$): at intermediate temperatures; H_2SO_4 determines reaction at 25°–30°. The extreme products are mixtures of tri- and higher acetates. (4) When the reaction mixtures are diluted with hydrocarbon, the fibrous cellulose may be acetylated without solution or sensible structural change.

Solvents of the higher acetates, are chloroform, acetone, phenol.

Saponification.—The acetyl groups may be removed by boiling with alkaline solutions, the cellulose being regenerated. In quantitative determinations the saponification may be effected by boiling with normal sodium hydroxide diluted with an equal volume of alcohol.

(*c*) **Acid-sulphuric esters.** By the action of sulphuric acid an extended series of esters is formed, which have been described as cellulose sulphuric acids. But they are certainly derivatives of products of resolution. The first stage results in the formation of a disulphuric ester $C_6H_9O_3(SO_4H)_2$, but its relationship to the parent complex is doubtful. The ester is soluble in water; the Ca, Ba, and Pb salts are insoluble in alcohol. By progressive hydrolysis the cellulose is ultimately resolved to dextrose.

(*d*) **Aceto-sulphates and mixed esters,** containing the SO_4H residues associated with acetyl and other negative groups in combination, are obtained when sulphuric acid is allowed to act under regulated conditions simultaneously with other esterifying agents. Thus a mixture of acetic anhydride (50 parts), glacial acetic acid (50 parts), and sulphuric acid (4–6 parts), acts rapidly at 30°–40°. The first product appears to be a neutral body of the empirical formula

$$(4C_6H_7O)SO_4(C_2H_3O_2)_{10}$$

and under the action of water to undergo an internal hydrolysis, the SO_4 group becoming SO_4H, which forms a stable combination with bases. The Mg, Ca, Zn salts are insoluble in water, but soluble in acetone.

(*e*) **Benzoates** result from the action of benzoyl chloride in presence of alkaline hydroxides. A monobenzoate (C_6) is obtained by treating cellulose with a solution of sodium hydroxide of 10 p.c. (NaOH) strength, and shaking with benzoyl chloride. This benzoate is formed with only slight structural change. The dibenzoate (C_6) is obtained by the interaction of benzoyl chloride and alkali cellulose (*mercerised cotton*) in presence of sodium hydroxide solution (15 p.c. NaOH). Its formation is attended by structural change; the fibrous cellulose is disintegrated, the dibenzoate being an amorphous substance. The dibenzoate is soluble in acetic acid, and chloroform.

Mixed esters, containing the benzoyl and nitric residues, result from the action of nitric acid upon the benzoates. Simultaneously a nitro- group enters the benzoyl residue.

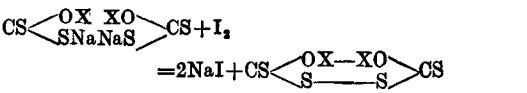
Alkali cellulose. The fibrous cellulose undergoes considerable structural modification under the action of solutions of sodium hydroxide of 12–15 p.c. NaOH. These reactions and phenomena were first studied by Mercer. They are the basis of the process of *mercerisation* (*q.v.*) under which cotton-yarn and cloth assume a special lustre and silky finish. There is a definite synthetical reaction in the ratio $C_6H_{10}O_5$: 2NaOH, which is a stage in the formation of the dibenzoate (*supra*).

The compound is completely dissociated by water; by treatment with alcohol an equilibrium is reached when the reagents are associated in the ratio $C_{12}H_{20}O_{10}$: NaOH.

The alkali-cellulose hydrate, of composition:

Cellulose . . 30 Sodium hydrate 15 Water . . 55	cellulose : sodium hydrate $C_6H_{10}O_5$ 2NaOH	

is the first stage in the synthesis of *cellulose xanthogenic* acid, which results from the interaction of the alkali cellulose and carbon disulphide at ordinary temperatures. The sodium salt is soluble in water. It is an unstable compound, the solution undergoing spontaneous progressive change. The solution, which is highly colloidal, finally solidifies. By means of the characteristic reaction of the xanthates with iodine



the progress of the change may be followed, the essential feature being the elimination of the CS_2 residues with reaggregation of the cellulose units. Well-marked stages in the series occur at the points denoted by the empirical formulæ $C_{12}H_{19}O_9CSSNa$, $C_{24}H_{39}O_{19}{\cdot}CSSNa$. The former represents an equilibrium attained after the solution has remained for some hours at the ordinary temperature; the latter is reached in from three to four days. The cellulose under the reaction acquires a more acid character, an additional OH group combining with alkali. The lower terms of the series, *e.g.* $C_{48}H_{79}O_{39}{\cdot}CSSNa$, though insoluble in water or dilute saline solutions, are dissolved by the addition of sodium hydroxide. The sodium atom in combination with the CSS residue is not attacked by weak acids such as acetic acid. By double decomposition with soluble salts of Cu, Zn, &c., the corresponding xanthates are produced as insoluble colloidal precipitates.

In the above reactions the cellulose aggregate is maintained; the solutions of the derivatives are viscous and colloidal; but in the following

B. **Reactions of decomposition,** which are determined by hydrolytic and oxidising agents, the directions of resolution are extremely various, and the relationships of the products to the original aggregate are undetermined.

(*a*) **Sulphuric acid** dissolves the cellulose as a disulphuric ester; but decomposition attends the reaction, and on diluting and boiling, the hydrolysis is carried to the extreme molecular limit, the final product being dextrose (*supra*).

(*b*) **Hydrobromic acid** in ethereal solution attacks the cellulose profoundly with production of brom-methyl furfural. The formation of this compound indicates a previous or intermediate stage in which the products of resolution are molecular ketonic bodies of carbohydrate constitution (Fenton, Chem. Soc. Trans. 1901, 361).

(*c*) **Hydrochloric acid,** in presence of water, dilute sulphuric acid, and acids generally, attacks the cellulose aggregate with production of a variety of derivatives. (1) *Insoluble*: these are generally termed 'hydrocelluloses.' They are disintegrated residues of the original fibres; they differ chemically from the parent aggregate in the presence of free aldehydic groups, and in readily yielding to the action of alkalis. (2) *Soluble* molecular products, chiefly dextrines and dextrose.

(*d*) **Alkaline hydroxides and alkalis** generally have little action on cellulose in the form of dilute solutions—even when treated at elevated temperatures. Sodium hydroxide in solutions of concentrations of 12 p.c. NaOH and upwards,

combines with the cellulose, producing profound structural modifications (mercerisation), but without resolving the aggregate.

At higher concentration and temperature the cellulose is partially dissolved; but even under the conditions of a 'fusion' at 180° the resolution is limited to the conversion into alkali soluble modifications, which are precipitated in the colloidal form on diluting and acidifying. At higher temperatures (250°) and with larger proportions of the alkaline hydroxides, the cellulose is resolved into acid products of low molecular weight, chiefly acetic acid and oxalic acid.

Oxidants. The directions of oxidation of cellulose are likewise extremely diversified. The aggregate manifests considerable resistance to alkaline oxidants in dilute form, *e.g.* solutions of the *hypochlorites*, *permanganates*; but when the limit is passed the oxidations which result are drastic in the sense that the soluble products are of low molecular weight, chiefly carbonic and oxalic acids. The insoluble fibrous residues, more or less disintegrated, are known as *oxycelluloses*. They contain free aldehydic groups, are easily attacked by hydrolysing agents, and on boiling with hydrochloric acid (1·06 sp.gr.) are decomposed with production of some furfural.

Resolved by the action of *concentrated* solutions of the *hypochlorites*, cellulose yields chloroform and carbon tetrachlorides. The hypobromites give the corresponding bromine derivatives. Nitric acid (1·25 sp.gr.) at 180° converts cellulose into a series of 'oxycelluloses,' which are resolved on boiling with calcium hydroxide into acid products, among which *iso*saccharinic and dioxybutyric acids have been identified. In the original oxidation small qualities of the higher dibasic acids—saccharic and tartaric acids—are produced, but the main products are oxalic and carbonic acids.

With *chromic acid* an endless series of oxidations may be effected, the degree of action depending upon the proportion of the active oxidant and the associated hydrolytic action of mineral acids. The oxycelluloses produced are distinguished by relatively large yields of furfural when decomposed by boiling HClAq. (1·06 sp.gr.). In presence of sulphuric acid there ensues complete combustion, and the reaction is the basis of quantitative analytical methods.

Resolution by ferment actions. Under the actions of specific organisms the cellulose complex is totally resolved, the main products being methane, hydrogen, and carbonic and fatty acids. The decomposition may be associated with the action of an enzyme; but a remarkable feature of the process is the absence of intermediate products, at least in the cases hitherto investigated. In the digestive tract of the herbivora, cellulose is resolved, and from the investigation of the process, necessarily by indirect observations, it appears that, in addition to a destructive resolution to ultimate gaseous products, there occurs a resolution to proximate groups of high nutritive value, which are assimilated by the animal organism.

Resolution by heat: destructive distillation. The decompositions of cellulose at temperatures exceeding 250° are necessarily extremely complex.

The groups of products show an average proportion:

Solid 30 p.c.	Liquid 50 p.c.	Gaseous 20 p.c.
Charcoal or pseudo-carbon	Containing acetic acid (2 p.c.), methyl alcohol (7 p.c.), acetone, furfural (12 p.c.)	Chiefly CO and CO_2

the actual proportions and composition of these mixtures varying with the temperature and duration of their heating.

General view of the decompositions of cellulose. It is clear that the cellulose complex breaks down under destructive influences, in directions depending upon the nature of the attacking agent, its concentration, and all the surrounding physical conditions. The study of these decompositions has thrown but little light on the actual nature and constitution of the cellulose aggregate; for the reason, perhaps, that we have endeavoured to maintain a basis of interpretation such as is applicable to ordinary molecular compounds or complexes. If we regard cellulose as the analogue of a complex salt in presence of water, and endeavour to follow the reactions of decomposition as we should the changing equilibrium of a *colloidal salt solution* under the action of reagents, we have a basis of working hypotheses which will be found to stand the general test of credibility—that is, they tend to progress in investigation. We make this observation in reference to the matter which we have just endeavoured to reduce to short, systematic expression, but which obviously cannot effectually be so treated because it involves the entire theoretical basis of our subject, that is, the actual state of matter and the distribution of the reactive unit-groups in the cellulose complex; and this basis is, as yet, entirely undetermined (*see* Cross and Bevan, Cellulose Researches, 1905).

The cellulose group. From the typical cellulose we pass to the diversified group of celluloses. Their general characteristics are those of the prototype; the variations they present are especially such as involve the undetermined factors of constitution. With these there are certain correlative variations which afford an empirical basis of classification. These are (*a*) the degree of resistance to hydrolytic and to oxidising agents; (*b*) the percentage yield of furfural when decomposed by boiling HClAq.; (*c*) elementary composition, in respect of the ratio C : O.

The fibrous celluloses are grouped as follows:—

Type	Cotton sub-group A. Bleached cotton	Wood cellulose sub-group B. Jute cellulose	Cereal cellulose sub-group C. Straw cellulose.
Hygroscopic moisture	6–8 p.c.	9–11 p.c.	10–12 p.c.
Elementary composition C	44·0–44·4	43·0–43·5	41·5–42·5
Elementary composition O	50·0	51·0	53·0
Furfural	0·1–0·4	3·0–6·0	12·0–15·0
Other characteristics	No active CO groups	Some free CO groups	Considerable reactivity of CO groups

Of these groups the following points may be noted :—

A. Comprises, in addition to cotton, other industrially important celluloses, *e.g.* flax, hemp, and rhea. They occur in the plant-world in association with compounds easily removed by the action of alkalis. They pass through the cycle of reactions involved in their solution as xanthates, without hydrolysis to soluble derivatives.

B. These celluloses are obtained as products of decomposition of a compound cellulose. They may be regarded as partially hydrated or hydrolysed. They are more readily attacked by hydrolysing agents and, in the xanthate reactions, are partially resolved to alkali-soluble derivatives.

C. These celluloses are in most cases a complex of structural elements, and not homogeneous chemically. They are still less resistant than the preceding group, and more especially the furfural-yielding components, which are selectively attacked under certain conditions.

The cellulose groups, as above, pass by imperceptible gradations into a heterogeneous class of natural products, which, while possessing some of the characterisitics of the celluloses proper, are so readily resolved by hydrolytic treatment that they must represent a very different constitutional type or types. To this group of complex carbohydrates the class-name *hemicellulose* has been assigned. They are structurally different from the fibrous celluloses, occurring mostly in the cellular form (parenchyma, &c.). They differ in physiological function, and in being readily resolved by hydrolysis into the crystalline monoses.

The foregoing *exposé* will enable us to group the *industrial and manufacturing applications of cellulose* in reference to first principles, as follows :—

GENERAL.—The uses of the fibrous celluloses, more particularly of cotton and the cotton group, in which we may include flax, hemp, and ramie, depend, apart from the primary condition of length of ultimate fibre upon the extreme chemical resistance of the fibre substance, which is a function both of the constitution of the ultimate groups and of their mode of union to constitute the aggregate itself.

Insensitiveness to oxidation is an obvious condition of such stability as is required for textile fabrics and paper, and, as evidence of resistance to atmospheric oxygen, we have the fact that flax and cotton fabrics and papers composed of these fibres have been handed down to us from antiquity, with little change. Next in order of importance is resistance to water and alkaline hydrolysis. This resistance enables textile fabrics to withstand periodical cleansing or laundrying, in which alkalis are the principal agents. In the purifying of textile fabrics by the bleaching processes and the preparation of paper pulps, the same negative qualities are of first importance.

Textiles are subjected to severe processes of alkali treatment, and to the action of bleaching agents, such as hypochlorites, without showing any chemical or structural modification.

On the other hand, there is a limit of the resistance to oxidation, and any undue action of the ordinary bleaching solutions leads to the formation of oxycellulose, and structural weakening as an attendant result.

While extremely resistant to alkalis, the celluloses are sensitive to acids, and here again in bleaching, finishing, and dyeing processes, the incidental acid treatments require careful adaptation to the limit of sensitiveness of the cellulose.

SPECIAL.—*Constitutional moisture and hydration effects* involve a range of phenomena of obvious industrial importance. The normal moisture of cellulose has to be taken into account in the finishing of textiles, and their package for shipment. The condition of the fibres as regards hydration, of which its capacity for combining with atmospheric moisture is an index, directly affects the finishing processes which are chiefly the mechanical operations of mangling, calendering, and beetling.

The further hydration of the cellulose which takes place in the beating operations of the papermaker are of considerable practical importance, and affect the quality and character of the papers in a very great degree.

Cellulose and ash constituents. The normal ash of the cellulose of the cotton group is small in proportion, and we are not able to affirm that these inorganic constituents have any determining relationship to the constitution of celluloses, though this is an accepted probability.

It is a problem for colloidal chemistry to establish this relationship in specific terms. Industrially, the question arises only with regard to the aggregate.

Thus in the purest form of cellulose in use, the filter paper used in quantitative separations by chemists, it is of importance that the ash components should be reduced to a minimum.

This minimum of 0·05 p.c. by weight, is attained by digesting the cellulose with hydrofluoric acid and hydrochloric acid, and thoroughly washing the paper in pure water.

Pure unsized cellulose paper thus treated constitutes the well-known 'Swedish' paper, so called from its country of origin, but now produced in Germany and other centres.

Cellulose as a typical colloid enters into characteristic combinations with inorganic oxides, and this property is an important basis of the processes of the dyer and printer.

Oxides of the polyvalent metals, notably of aluminium, chromium, iron, tin, and lead, are taken up by the celluloses from solutions of their salts, and the cellulose thus *mordanted* has increased special affinities for colouring matters.

A more special industrial application of this property is the method for making the mantle, now in common use, for intensifying coal-gas illumination (Auer-Welsbach). The colloidal oxides of thorium and cerium in suitable proportions are fixed upon cellulose fabrics, which are then dried and ignited. The result is an inorganic skeleton of the original fabric, prepared in any desired form, and composed of the oxides in question.

The particular form fulfils the conditions of maximum illuminating surface, together with the desired degree of mechanical resistance to stand wear and tear under the particular conditions of employment.

Cellulose and solvents. It is in the solutions of cellulose or its derivatives that the particular properties of the cellulose aggregate are evident.

In the case of the aqueous solvents observation shows that the cellulose, employed as fibre, passes through phases of progressive hydration with considerable distension until the final stage of homogeneous structureless solution is reached.

The general character of the solutions is their high viscosity, which imposes a limit of from 7 to 9 p.c. cellulose for solutions which require filtering.

The technical applications of these solutions depend upon the fact that the cellulose is brought into the plastic homogeneous structureless condition, in which it may be formed or shaped at will, and in finally reverting to the solid state preserves its structural continuity through the successive phases of dehydration.

The solution in zinc chloride has been used for making threads to be carbonised for electric incandescent lamps.

The solution is forced through narrow orifices into alcohol, which precipitates the cellulose as a transparent hydrated solid, retaining zinc oxide (hydrate) in combination. The solid hydrate is formed and manipulated in continuous length, and, when freed from zinc oxide and dried, is a structureless cylinder of cellulose. Heated out of contact with air, it is converted into a 'pseudo-carbon,' which constitutes the filament in question.

The solution of zinc chloride in hydrochloric acid has been employed for converting cellulose papers into a special agglomerated product or board, which is used as an insulating material and for structural purposes. The sheets or webs of paper are treated with the solvent by immersion, and the material thus attacked is then welded into the composite fabric by means of the adhesion of the viscous cellulose solution resulting from the attack.

The composite sheets or webs so produced are finally compacted by pressure, and then exhaustively washed to remove the solvents.

Cuprammonium. There are various industrial applications of this characteristic solvent. Textile materials are treated by passing through the solution. The cellulose is attacked superficially, and under the pressure of rolls the gelatinised product is distributed uniformly: the fabric is then dried. The fabric is thus coated with a varnish composed of cellulose and the hydrated copper oxide, of greenish colour which renders the fabric impervious to water and rot-proof.

Papers are similarly treated; the sheets or webs being welded together under pressure. These fabrics have been known for a number of years as the 'Willesden' waterproof fabrics.

The most important industrial application of the solution is in the manufacture of artificial cellulose threads, which are produced in various grades of fineness, and known as 'Artificial Silk,' 'Monofil' (Lustra Cellulose, Soie Artificielle, Glanzstoff, Crin).

The process in its simplest terms consists of the production of the solution by treating bleached cotton with the cuprammonium solvent, and filtering through fine metal-wire cloth to remove incidental impurities.

The solution is projected through orifices of varying diameter, according to the size of the threads to be produced, into solutions which precipitate or coagulate the cellulose.

The setting solutions are of two types, acid and alkaline.

The cellulose is precipitated as a hydrated solid, in continuous length, and is drawn forward at speeds varying from 20 to 50 metres per minute, according to the diameter of the thread and the conditions of the precipitation.

In the case of fine filaments, constituting artificial silk, several of the threads so produced are twisted together to form a compound filament or yarn suitable for weaving purposes. The products are dried under special conditions, to secure maximum lustre and elasticity.

Cellulose esters. The application of the nitrates to high explosives is an application of cellulose that stands apart and depends, of course, upon the fundamental chemistry of the product.

The ratio of oxygen is such that the products contain the elements for their complete conversion into gaseous products when raised to the reactive temperature.

The nitrates in the fibrous form in which they are produced, are explosives of the disruptive or blasting type, and were exclusively so used for many years.

The type of explosion required for the propulsion of projectiles, is a restrained or graduated combustion, which is determined by a change of form of the nitrates. These are convertible into plastic modifications under the action of their specific solvents, and in this state they may be formed or fashioned into threads, cylinders, or solids of any desired form or dimension. The combustion of these structureless solids, in its aggregate explosive effect, may be made to fulfil any desired conditions.

The most interesting case is that of the employment of nitroglycerine, itself a high explosive, and the basis of dynamite, to reduce the cellulose nitrate, acting as a solvent, to the structureless condition.

Mixtures of nitrocellulose and nitroglycerine, in suitable proportions, are drawn to threads and constitute with certain admixtures the modern explosives cordite, ballistite, &c. (*see* EXPLOSIVES).

The cellulose nitrates, treated with neutral solvents and subject to a process of milling, are reduced to a structureless plastic mass. This may be reformed into solid substances which may be produced in any desired form or dimension. In sheets or film they constitute the basis or transparent carrier of photographic emulsions.

In solid form they are known as celluloid, xylonite, &c., and find endless applications both useful and ornamental (*v.* CELLULOID).

The solutions of nitrates in neutral solvents, such as ether-alcohol (collodion) or amylacetate, are used as varnishes and lacquers for various purposes.

The cellulose nitrates in ether-alcohol solution are employed industrially in the manufacture of artificial silk.

This, in fact, was the pioneer invention 'of Chardonnet,' and dates from 1883. The process of spinning consists in forcing the solution through capillary glass jets, either into air (Chardonnet) or into water (Lehner).

The thread is thus formed and obtained as

a nitrate, in which form it is twisted into compound textile filaments, which are reeled into skeins of yarn.

Process of saponification for removing the nitric groups follows. This consists in digesting the nitrate yarn in solutions of ammonium-magnesium sulphydrates at ordinary temperatures.

As a result of the cycle of operations, the denitrated cellulose as obtained constitutes the artificial silk of commerce.

Cellulose acetates are the analogues of the nitrates with the radical distinction of being non-explosive, and, in fact, eminently stable compounds.

By treatment with their special solvents, they are dissolved to homogeneous viscous solutions, and they may be fashioned into films and solids as are the nitrates.

So far the industrial applications of the acetates have been limited chiefly by the prohibitive costs of production.

A new technical departure, however, to overcome this difficulty is embodied in patents of Knoll and Knoevenagel (1905–1910), which describe processes for preparing a *normal tricetate* in stable form, and the properties of which are such that the solution may be used directly as obtained, and without any processes of separation, purification, and resolution of the acetate.

This solution, which is a solution in acetic acid, is coagulated by water, and continuous solids are therefore produced by forcing the solution (through orifices of suitable dimensions) into water. The acetic acid may be recovered from the precipitating bath by simple means.

Cellulose acetate has already been spun to artificial silk and the coarser textile threads, but there has been so far no industrial development of the processes.

The technical interest of such a product is that it is employable as an ester, whereas, of course, the nitrate is entirely unsuitable, as such, for textile applications.

Cellulose and alkalis (Mercerisation). The action of alkaline hydroxide in strong solution (15–20 p.c. NaOH) upon cotton textiles, is the basis of a special industry. By converting the cotton fibre into the modified form, cotton yarns and fabrics are changed in appearance and acquire a silky lustre and touch.

The goods to be 'mercerised' are passed through a solution of caustic soda in the cold. This produces the effect of considerable shrinkage accompanying the change of form and dimensions of the ultimate fibre, from a flat membranous, to a thick-walled cylindrical homogeneous tube.

This shrinkage is resisted by placing the goods under the condition of mechanical strain, either during the process of alkaline treatment, or, after allowing the shrinkage to take place, the goods may be afterwards stretched to their original length.

The fundamental observations which condition this process were made by J. Mercer (1850–1860), but they remained undeveloped until late in the century (1880–1890).

The industry is now a considerable one, and is to a certain extent independent of fashion (*see* MERCERISING).

Cellulose and sulphuric acid. Whereas cellulose reacts with the more concentrated acids (H_2SO_4—H_2SO_4,H_2O) to form sulphuric esters, the acids of 67·0 to 78·0 p.c. H_2SO_4 (approximately H_2SO_4,$2H_2O$—H_2SO_4,$3H_2O$) hydrate, and dissolve the cellulose to a colloidal solution, from which, if immediately diluted, the cellulose is precipitated as a gelatinous hydrate ('Amyloid'). These reactions are industrially applied in the preparation of 'parchment paper,' or 'vegetable parchment.' A pure cellulose paper is passed through a bath of acid, and immediately, in continuing length, into water, which arrests the action of the acid and reprecipitates the cellulose superficially dissolved as a structureless colloid. After washing from the last traces of acid, the web of now parchmentised paper is dried under special conditions of strain to control the shrinkage of width (10–13 p.c.), so as to maintain an even surface and prevent deformation. To overcome the brittleness of the product, which would result from total drying, it is treated with solutions of neutral hygroscopic substances, such as glycerol or glucose, before passing on to the drying cylinders. A sufficient proportion is retained in the finished product to ensure a normal 'humidity.'

The total hydrolysis of cellulose to dextrose is effected by dissolving in the more concentrated acid, and, after allowing the acid to act until the solution becomes limpid, diluting and heating the dilute solution. The acid is neutralised with chalk, filtered from the insoluble calcium sulphate, and concentrated. The industrial value of this process is obviously limited by the relatively low values of starches and the more economic conversion of these by simpler means and to superior products.

Physiology of the compound celluloses (Vegetable fibres). While the simplest form of vegetable life is the cell, and the cell is, moreover, the universal originating unit, we observe, as we ascend the scale of plant organisation, an increasing variety of differentiations of this simplest structural unit graduating into the fibres and vessels of the stems of the higher flowering plants. It is to the presence of such elongated cells as warrant the designation 'fibre' that these stems mainly owe their powers of bearing strains and resisting fracture. The uses to which these fibres are put in the arts obviously depend upon the same characteristics of form, as well, of course, as the nature of the fibre substance. So too the anatomy of fibrous stems is necessarily a main factor of the processes by which they are treated for the isolation of the fibres. We must here except from the general anatomical view we are about to take the most important of the vegetable fibres, viz. cotton, which as a seed hair is distinct physiologically, and differs structurally from all other fibres employed for textile purposes.

The 'ultimate' fibre is a hollow tube, the walls being thin and membranous; it is attached at one end to the testa of the seed, the other being free, and there is no adhesion of the fibres to one another. The preparation of the textile fibre involves, therefore, only a mechanical treatment, and that of the simplest kind, for separating it from the seeds. The other vegetable fibres employed in the arts are without exception constituents of complex structures (stems and

leaves) which require a more elaborate mechanical operation for their separation, in addition in many cases to a preparatory chemical treatment.

The fibres of stems are arranged according to the two main structural types of growth, the exogenous and endogenous. In the exogenous stem of annuals (dicotyledonous) they constitute a localised tissue, the bast, which is an annular ring external to the wood and beneath the cortex. In the endogenous stem the fibres proper (bast fibres) are generally aggregated together with vessels into bundles known as fibro-vascular bundles, which are scattered more or less irregularly throughout the cellular matrix.

In regard to the leaf, the two great divisions of the phanerogams are also contrasted; the fibro-vascular bundles of the former are not only irregularly disposed, but interlaced (reticulate venation), whereas the leaves of the typical monocotyledon are characterised by a parallel arrangement of the bundles, and fulfil, therefore, a necessary condition of separation for textile purposes. Fibres of this class are amongst the most useful that we have. There is a distinction to be noticed, though rather of a technical than anatomical nature, between the vegetable fibres and 'fibrous substances.' By the former we understand isolated bast fibres or fibro-vascular bundles, such as can be *spun* into a continuous length or yarn. A fibrous substance is, of course, any vegetable structure containing fibres. Many of these do not admit of being economically treated for the isolation of a textile fibre, but, on the other hand, are resolved by suitable *chemical* treatment into a fibrous mass or *pulp*, available for paper making. Many of our most valuable raw materials for this industry are of this nature. We may further distinguish, according to the above classification, (1) exogenous bast tissues, such as those of the Adansonia and Broussonetia (paper mulberry) and entire stems (woods); and (2) endogenous stems (straws and bamboo), and leaves (esparto). In this more miscellaneous group also we should include the refuse from the preparation of textile fibres, such as the root ends of jute (butts), the waste from the flax-scutching process (*infra*), &c.

We have already excepted the cotton fibre from the above classification, indicating a structural as well as a physiological distinction from other textile fibres. These are, in fact, always obtained and spun in the form not of *ultimate* fibres, but of bundles of these. The ultimate bast fibre is also a hollow tube, but more or less thick walled and with tapering extremities; in section it is seen to be cylindrical or polygonal. The dimensions are remarkably uniform for the bast of any given plant or species, but exhibit wide variations from species to species. Thus the average length of the bast cell of jute is 3 mm., and of flax 28 mm. The textile 'fibres' are aggregates of these ultimate fibres, and it is convenient to employ for them the special designation of *filament*. This complex spinning unit varies in the number and degree of cohesion of the constituent fibres. These variations even in the same plant or species are very considerable, but more so as we pass from species to species. Expressed in another way, the textile fibres vary very much in regard to fineness and divisibility of the filaments. These, it is scarcely necessary to say, determine in a very important sense their spinning qualities. The nature of the fibre substance is a self-evident factor of the mechanical properties of the filaments; and lastly, though less obviously, the length of the *ultimate fibre*, which greatly influences the strength and durability of the yarn.

To the spinner the chemical composition and properties of the fibre substance may appear of altogether secondary importance; but they are obviously of first importance in regard to the application of the yarn, as of the goods woven from it. Supposing them put into use without further preparation, the durability of the fabrics will depend upon their resisting the disintegrating action of air (oxygen) and water, reinforced by heat and light. But a large proportion of the textile fabrics of commerce are supplied to the consumer in the bleached state, the process of bleaching consisting in the removal, by a more or less drastic treatment with reagents of those fibre constituents to which the colour of the raw material is due. These processes being the subject of a special article, we shall not require to deal with them at all in detail. The principles underlying them, however, have a close and obvious connection with the properties of cellulose, and the relationships subsisting between the cellulose of the vegetable fibres and the non-cellulose constituents with which each is associated in the plant; and from this point of view we proceed to give a short account of the

Chemistry of the Compound Celluloses.

There are many reasons for regarding cellulose and the non-cellulose constituents of vegetable tissues and fibre substances as united chemically. Taking cellulose as the constant, the basis of our classification of the compound celluloses will be the nature of the non-cellulose, the characteristics of which are as distinct as they are general. Physiologists recognise three 'modifications' of cellulose in the plant, and these we term 'compound celluloses.' We shall find the distinguishing chemical features of the three groups of compound celluloses as well marked as their functional correlations, and the corresponding classification has a 'natural' in addition to its 'chemical significance.' We shall consider first the group which is of least, because of only incidental, importance in relation to our subject.

Cutocelluloses (Adipocelluloses). The protective tissues of plants, which are, moreover, cellular rather than fibrous, viz. cork and cuticle, are composed of a substance of marked water-resisting characteristics. In this property, as well as in empirical composition, the cuticular substance designated *cutose* by Fremy resembles many of the waxes. The following percentage numbers are the results of the analysis of the cuticle of the apple purified from wax and adventitious matters: C, 73·66; H, 11·37; O, 14·97.

Cork is not a simple substance, but contains a number of products, wax, fatty esters and anhydrides, proteid residues, and tannins, &c., associated with the matrix or skeleton substance,

which is of the nature of *cutose*. Both cutose and cork yield a residue of cellulose when treated with special reagents (sulphites) for the resolution of its union with the wax-like non-cellulose. The latter[1] is resolved by boiling with strong solutions of the alkalis into two fatty acids, a solid acid designated *stearocutic* and a liquid called *oleocutic acid*. The investigation of these cuticular substances has not been sufficiently extended to warrant our entering into further detail in regard to their composition and properties. We may regard them as compound celluloses resolved by alkaline saponification into cellulose and a mixture of fatty acids of peculiar properties, but altogether unknown constitution. They may be conveniently grouped under the term *adipocelluloses*, which broadly expresses their chemical relationship. As regards their distribution, they occur chiefly in the epidermal and cortical tissues of leaves and stems, but the observations of Fremy lead to the conclusion that they are by no means confined to these, and there is evidence of their presence, if only in minute proportions, in the fibres themselves; but their occurrence, chemically speaking, may be regarded as adventitious, the fibre substances belonging to essentially different classes of compounds. These adipocelluloses, moreover, in most of the technical applications of vegetable materials which come within the province of this article, have to be got rid of. An instance of an epidermal tissue (cutocellulose) used as such is the Raffia, which consists of the cuticular tissues of *Raphia ruffia*. This 'fibre,' in horticultural work, replaces the 'bast' or 'bass' of a former age. When the fibres themselves are isolated, this is accomplished for the most part by the mechanical processes of preparation, scutching, hackling, &c. When, however, the tissue intervening between the fibres and the cortex or epidermis is of small extent, the separation is never complete. In flax, for instance, residues of the epidermal tissue remain associated with the fibre, and the relative difficulty of attacking these substances by chemical means is a factor of the laborious process of bleaching linen goods. In isolating the so-called New Zealand 'flax' much greater difficulty is experienced. This fibre consists of the fibro-vascular and other fibre bundles of the sword-shaped leaf of the *Phormium tenax*, and these are in such close and intimate contact with the epidermal tissues that their isolation is always very incomplete. In those raw materials of the paper maker which consist of the stems and leaves of monocotyledons (straw and esparto), the epidermal adipocelluloses constitute a sensible proportion. They are resolved in this case by chemical means, which require to be much more drastic in consequence. The fibrous portions of these materials, on the other hand, are made up of a compound cellulose belonging to the next group which we shall have to consider, an important characteristic of which is the comparative ease with which they are attacked and resolved by alkalis. Although, therefore, the connections of these cuticular celluloses with the fibres are for the most part only indirect or incidental, we see in the typical instances above cited that they have to be taken into account in relation to a great number of the treatments of cellulosic raw materials, both mechanical and chemical.

[1] According to Fremy, it is the cutose itself which is so resolved, but the author's experiments have always yielded a residue of cellulose.

Pectocelluloses. This, the second division of the compound celluloses, is characterised by the non-cellulose constituents belonging to the group of *pectic* substances or pectins. The pectins are carbohydrate-colloidal aggregates or complexes of hexoses and pentoses, with a small proportion of acid groups combined as lactone or ester. Sensitive to acid hydrolysis and ferment actions, they occur naturally in the most varied forms. Thus in fruit juices they exist as colloidal ropy solutions. In the non-permanent fibroid tissues they are insoluble in water (Tollens, Annalen, 286, 278–292; Cross, Ber. 1895, 2609).

In composition they are more complicated than the celluloses, and they contain less carbon and more oxygen. In this and in many of their properties they resemble the oxycelluloses above described. Generally, they yield gelatinous hydrates, and under the action of hydrolytic agents they undergo a succession of changes resulting in the conversion of the comparatively inert members of the series pectose and pectin into highly acid derivatives, such as pectic and metapectic acids, bodies which, in addition to being acids, have properties indicating the presence of aldehydic groups.

The typical pectocellulose is the flax fibre. The purified bast of a Russian flax was found by Kolb to contain C, 43·7; H, 5·9; O, 50·4.

On boiling with dilute alkaline solution about 20 p.c. of its substance is readily converted into soluble derivatives, of which a considerable proportion is a body identical with Fremy's pectic acid (C=42·0 p.c.; H=4·8; *i.e.* $C_{16}H_{22}O_{15}$). The fibrous residue from an exhaustive treatment with alkaline solutions, amounting in most flaxes to about 75 p.c. of the original weights, is a practically pure cellulose. In this experimental account of its constitution we disregard such adventitious admixtures as cuticular tissue (adipocellulose) and wood or 'sprit' (lignocellulose), the influence of which may be calculated and eliminated from the result; but the presence of these in commercial flax introduces complications of very great moment in regard to the spinning of the fibre and the bleaching processes to which flax goods are subjected. In regard to the latter, an important technical difficulty is experienced in washing flax yarns after a 'chlorine' (hypochlorite) bleaching treatment. 'Active chlorine' remains persistently in the goods. This is now elucidated, as due to the formation of *chloramin* derivatives, from residues of chlorophyll and other nitrogeneous products containing amino- groups always present in cuticular tissues (Cross, Bevan, and Briggs, J. Soc. Chem. Ind. 27, 1908).

Lignocelluloses. As the name indicates, this group comprises the substance of the ground tissue of the woods. The simplest type of lignocellulose, chemically as it is structurally, is the jute fibre, the lignified bast of an annual (*Corchorus tibiaceæ*) cultivated on an enormous scale in India, and the staple of an important textile industry centred in Dundee.

The elementary composition of the purified

fibre is expressed by the following percentage numbers :—

	Calc for $C_{12}H_{18}O_9$
C = 47·0–46·0	47·0
H = 5·9–5·7	6·0
O = 47·1–48·3	47·0

The constitution of a lignocellulose is revealed by the action of chlorine, which combines with the non-cellulose or lignone component to form a quinone-chloride of constant composition, $C_{19}H_{18}Cl_4O_9$. This body reacts with sodium sulphite (solution) to form a sulphonated derivative of characteristic magenta-red colour, freely soluble as sodium salt; consequently, the chlorinated fibre is resolved by treatment with solution of sodium sulphite (2 p.c. Na_2SO_3), the lignone-chloride dissolving from the cellulose, which is thus isolated. The quantitative constants of this reaction, which is of fundamental importance, are as follows :—

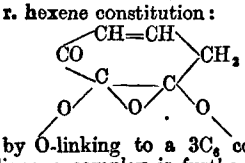
	P.c. of lignocellulose
Chlorine combining with lignone .	8·0
,, ,, as HCl . .	8·0

And the lignocellulose may be statistically represented as composed of :

	P.c. of lignocellulose	Carbon
Lignone $C_{19}H_{22}O_9$[C=57·8 p.c.]	20·0	11·56
Cellulose $C_6H_{10}O_5$[C=44·4 p.c.]	80·0	35·52
	100·0	47·08

The cellulose is separated actually as a hydrate of the composition $3C_6H_{10}O_5,H_2O$. It further differs from the normal cotton cellulose in being non-homogeneous. It is a mixture of two celluloses, the α-cellulose approximating to the normal (65 p.c.) and β-cellulose (15 p.c.); the latter being relatively sensitive to hydrolysis and yielding a large proportion (40–50 p.c. of its weight) of furfural on boiling with condensing acids.

Constitution of lignone. The characteristic groups of the lignone complex are those which combine with chlorine and which appear to be of keto r. hexene constitution :



united by O-linking to a $3C_6$ complex. The entire lignone complex is further characterised by containing $O.CH_3$ groups, and a residue which is easily hydrolysed by both acids and alkalis to acetic acid (5–7 p.c. of the lignocellulose). This indicates hexene groups and their proportion of the lignone to be large.

The wood substance of perennial woods (dicotyledons) with the same general characteristics differs in the relation of lignone to cellulose, both in proportion and in mode of union. Whereas the jute fibre is attacked by solvent reagents similarly to the celluloses, the woods are extremely resistant. The following comparison of typical constants for beechwood is noteworthy :—

	Elementary composition		Proximate composition		Quantitative reactions of lignone		
	C	H	cellulose	lignone	methoxyl	furfural	chlorine combining
Jute	47·0	5·9	80	20	4·6	8·0	8·0
Beech	49·1	5·6	55	45	6·2	12·8	12·0

The wood substance of the *Coniferæ*, first investigated by Erdmann (Ann. Suppl. 5, 223), is a homogeneous complex—lignocellulose—of empirical composition, $C_{30}H_{46}O_{21}$, differing in minor respects from the woods of angiosperms chiefly in the lower proportion of 'furfuroid' and acetyl groups. A reaction of fundamental import and general for the entire group of lignocellulose, is the basis of the 'bisulphite' process of preparing cellulose from woods, applied chiefly to the coniferous woods, the insoluble residue of disintegration of cellulose constituting the most important staple of modern paper making. The lignone complex reacts quantitatively with the disulphites to form derivatives of the empirical composition $C_{24}H_{23}(OCH_3)_2O_3{\cdot}SO_3H$; the mechanism of the reaction being : (1) a hydrolysis of 'acetal' groupings due to combination of H·CO and bisulphite residues; (2) the SO_3H residues then migrating to unsaturated —CH=CH— positions; the lignone complex being thus obtained as lignone sulphonates (Ca or Mg salts), which are gummy deliquescent solids.

These reactions take place progressively in the range of temperatures 80°–150°, and industrially are carried out in digestors of special construction (silicate-lined) and enormous capacity.

A third reaction characteristic of the lignone complex as such and taking place in definite quantitative proportions is its condensation with phloroglucinol in presence of HClAq. There are two phases of the reaction : (1) with formation of a crimson colouring matter. This takes place with a proportion of the phenol less than 1 p.c. of its weight. The depth of colour is quantitatively related to the lignone, and is, therefore, an approximate measure of its proportion in a lignocellulose, as of lignocellulose (*e.g.* 'mechanical' wood pulp) in admixture with cellulose. (2) A further combination with the phenol (6–7 p.c. of its weight) to a product which is extremely resistant to hydrolysis (Cross, Bevan, and Briggs, Ber. 40, 3119).

Characteristic colour reactions are those with aromatic bases; the anilines giving yellow to orange-colouring matters. Dimethyl-*p*-phenylenediamine give a deep-red colouration, which is the basis of the well-known quantitative method of estimating lignocelluloses in mixtures (C. Wurster).

Ferric ferricyanide in solution is reduced by the lignocelluloses, and the intermediate ferroso-ferric blue cyanides in the highly hydrated colloidal form, are precipitated upon the fibre substance in intimate 'adsorption' combination. Jute fibre will take up from 30 to 50 p.c. of its weight of the blue pigments thus formed, without any change of essential characteristics. These phenomena have especial interest in relation to theories of dyeing and the colloidal state (Cross and Bevan, J. Soc. Chem. Ind. 1893, 12, 104), and are of use in laboratory investigations of plant products (Sherman, J. Amer. Chem. Soc. 1897, 291).

The lignocelluloses have many-sided affinities for colouring matters, due to specific reactivities of the constituent groups of the lignone complex. They are dyed directly by dyestuffs of the most varied constitutional types; and in this respect stand in marked contrast with the celluloses,

which present a narrow and selective range of direct tinctorial capacity.

Other less characteristic reactions of the lignocelluloses may be briefly described.

Halogens. Bromine reacts to form brominated lignone derivatives; but the attack is much feebler than with chlorine, and is complicated by oxidations. Cellulose is isolated by repeated treatments with bromine water, followed by dilute alkalis. This is a useful quantitative method of cellulose estimation (Hugo Müller, Pflanzenfaser). Iodine is absorbed from its aqueous solutions (in KI) in definite proportions. Jute fibre digested at 18° with 20 times its weight of N/10 solution as ordinarily prepared, absorbs 12·9–13·3 p.c. iodine (Cross and Bevan, Cellulose, 138, 139).

Hydrolytic agents generally attack the lignocelluloses as a whole, that is, without resolving the lignonecellulose combination. At elevated temperatures (100°–160°) dilute alkalis (NaOH, Na_2S) selectively attack the lignone groups, breaking them down to acid products—acetic acid, and the so-called lignic acids—which dissolve as sodium salts, and cellulose is obtained as a residue.

Dilute acids at higher temperatures yield acetic acid as a product of hydrolysis (Cross and Bevan, Cellulose, 160, 161; W. E. Cross, Ber. 1910, 43, 1526), and a complex of products of condensation, including furfural.

Oxy-hydrolytic agents attack the lignone complex owing to its unsaturated and oxidisable characteristics. By the action of nitric acid even in dilute form (5–10 p.c. HNO_3) and at low temperatures (70°–80°) the lignone is resolved into gaseous and soluble products; the β-cellulose components are also attacked, and a residue of α-cellulose is obtained, but more or less oxidised to oxycellulose.

It is noteworthy that in presence of urea the action of nitric acid loses its specific character and resembles that of the simple hydrolysing acids (Cross and Bevan, Cellulose, 141, 145).

Chromic acid in presence of hydrolysing acids oxidises the lignone to oxalic and carbonic acids. Acetic acid appears as a product of hydrolysis. The insoluble residue is an oxycellulose soluble in large proportion in dilute solution of sodium hydroxide.

Permanganates in sufficient proportion oxidise the lignone complex to products of low molecular weight, but the action may be regulated and graduated to produce valuable bleaching effects.

Hypochlorites are used in industrial bleaching operations (jute yarns and fabrics), but require most careful control to prevent chlorination of the fibre substance, the fixation of chlorine, even in minute proportion, leading to ultimate disintegration of the lignocellulose (Cross, Bull. Mulhouse, 1883).

Ultimate oxidations. By 'fusion' with the alkaline hydroxides at 250°–350° the lignocelluloses are oxidised to oxalic acid, the yields from the wood (sawdust) being large (80 p.c.). The process is of considerable industrial importance, being the main source of the oxalic acid of commerce.

By chromic acid in presence of sulphuric acid the lignocelluloses are oxidised to gaseous products (CO_2 and some CO) and water. The reaction is the basis of a quantitative volumetric method of estimation.

Synthetical reactions. Esters. The lignocelluloses react, as do the celluloses, to form nitrates, acetates, and benzoates; these, however, are mainly reactions with the cellulose of the complex, the lignone groups containing no reactive OH groups: these remain in condensed combination in the resulting ester complex.

The xanthogenic ester which results from the successive action of sodium hydroxide (17·5 p.c. NaOH solution) and carbon disulphide is a mixture or series of products, partly soluble, partly a highly hydrated and distended fibrous colloid which may be separated by filtration. There is no resolution or separation of the lignone groups from the cellulose.

Destructive distillation. The highly complex changes which the lignocelluloses undergo when heated out of contact with the air, are only approximately accounted for in terms of the original substance. Typical of an enormously diversified series of volatile products are:

Methyl alcohol	Methyl furfural
Acetone	Methyl- and methoxy-derivatives of Pyrogallol
Acetic acid	
Furfural	

which may be regarded as direct products of resolution of the lignone complex.

Of great industrial importance are the products of the first group. The solid residue (about 50 p.c.) is wood charcoal, a highly condensed 'pseudo-carbon' of the approximate elementary composition, $C_{20}H_{18}O_4$.

Autoxidation of lignocelluloses. Lignocelluloses in the form of ground wood or 'mechanical' wood pulp are largely used in modern printing papers. Such papers are not only inferior in physical quality—tensile strength and elasticity—but in permanency; they change in colour (to yellow and brown) and in structure, becoming brittle. These are primarily effects of oxidation; they are influenced by light, and by catalysts such as iron compounds usually present in papers as an incidental impurity, and resin acids added as sizing agents. These effects and defects are generally recognised and lead to the specific exclusion of 'mechanical' pulps from papers intended for documents of permanent value (Report of Society of Arts Committee on Deterioration of Papers, J. S. A. 1898).

An important elucidation of these phenomena is suggested by the researches of the late W. J. Russell, described in the Royal Society papers on The Action of Wood on Photographic Plates in the Dark (Phil. Trans. (B), 1904, 197, 281; Proc. Roy. Soc. 78, 385; 80, 346). The action in question is a 'photographic' image reproducing the structural details of the wood sections, placed at some distance from ordinary sensitive plates, but with exclusion of light.

On the evidence, the effects are due to an 'active emanation' from the wood substance, which appears to be a product having the characteristics of hydrogen peroxide. The general evidence also connects the phenomena with those of autoxidation, and these again with the constitution of the lignone groups of the wood substance.

Assay of Fibrous Materials.

For the investigation of fibrous raw materials in the laboratory the following scheme, devised by the author (Ind. and Col. Exhibition Reports, 1887), has been generally adopted:—

Separate portion taken for each determination.

Results calculated in percentage of dry substance.

1. Moisture:
   Hydroscopic water, or water of condition, loss on drying at 100°.
2. Ash:
   Total residue left on ignition.
3. Hydrolysis:
   (*a*) Loss of weight on boiling 5 minutes in 1 p.c. solution of caustic soda;
   (*b*) Loss of weight on continuing to boil one hour.
4. Cellulose:
   Isolation and estimation as previously described (chlorination method).
5. Mercerising:
   Loss of weight on treating one hour with strong solution of caustic soda, 15–20 p.c. NaOH, in the cold.
6. Nitration:
   Weight of nitrated product, obtained by treatment with mixture of equal volumes of nitric and sulphuric acids one hour in the cold.
7. Acid purification:
   Loss of weight after boiling with 20 p.c. acetic acid and washing with water and alcohol.
8. Carbon percentage:
   Determined by combustion.

1*a*. *Moisture.* The mere operation of drying at 100° determines molecular changes in such compounds as the lignocelluloses, changes which affect the subsequent action of reagents. It is necessary, therefore, to weigh separate portions for the particular experiments in the air-dry condition, and calculate the dry contents from the data of the specimen weighed after drying at 100°. The dried specimen is treated for 1*b* *Fat, wax,* and *resin.* These constituents are estimated as an aggregate extract obtained by boiling out with hydrocarbon solvents, or with ether-alcohol.

2. *Ash.* The specimen weighed after extracting may then be burned for the determination of ash. The ash in isolated fibres is low, viz. 1–2 p.c.; in fibre aggregates it is often high, thus in esparto and straw from 3–6 p.c., and should be taken into account in calculations of yields or loss of weight. In such cases, after weighing the product of any given reaction the specimen or a portion of it should be burnt and the ash determined. The ash-free product is calculated in terms of the original substance, also taken ash-free.

The ash constituents are: (1) those of the normal fibre; and (2) in certain cases adventitious mineral matter. These are easily distinguished and separately estimated.

3. *Alkaline hydrolysis.* This is the first stage towards the isolation of the cellulose. When the numbers obtained for the short period (*a*) and for the long digestion (*b*) show a marked difference, it is an obvious general indication of low paper-making quality.

4. *Cellulose.* Having isolated a white residue from a raw fibrous material, it may be weighed and then further investigated. An estimation of furfural will establish its position in the classification of the celluloses. For practical purposes it is sufficient to establish the degree of resistance of the cellulose to further alkaline hydrolysis, and to oxidation by alkaline cupric oxide (Fehling's solution).

5. *Mercerising.* The effect of the action of caustic soda as measured by loss of weight, and also changes in appearance and structure, may be usefully observed on the isolated celluloses, and in certain cases upon the raw fibrous materials. The pectocelluloses are considerably gelatinised by the treatment, the fibres often undergoing agglomeration and drying to a harsh wiry condition. The lignocelluloses are affected in the contrary direction. The cutocelluloses are not attacked.

From all the above treatments the products should be treated with dilute acids by immersion in the cold, and copiously washed before drying. The drying is accelerated by treatment with alcohol.

6. *Nitration,* or conversion into nitric esters, affords useful information; but judgment must be exercised as to the applicability of the treatment to the raw material, to the partially purified products (alkaline hydrolysis), or the isolated cellulose. It is a general measure of the proportion of reactive alcoholic OH groups, and also of resistance to oxidation.

7. *Acid purification* removes basic mineral matter, often present in some quantity in raw materials, of the pectocellulose class. It may sometimes be required to attack and remove more resistant mineral constituents, such as silica or silicates. In this case the material may be digested with a mixture of hydrofluoric and hydrochloric acids in vessels suitably resistant to the action of these acids. The treatment is followed by copious washing.

8. *Carbon percentage.* This is only necessary in certain investigations. The value of the constant will be recognised from the fact that it varies considerably for the different groups of compound cellulose. The most convenient method is that of combustion, with chromic acid, after solution in sulphuric acid.

For special purposes the above scheme is extended by operations on a larger scale, and under conditions which approximate to those industrially employed, as, for instance, in estimating the value of a raw material for paper-making purposes: complementary investigation of structural characteristics, including the measurements of length and diameter, of ultimate fibres (cellulose) is also required. For processes and methods the special text-books must be consulted.

The following is a general view of the

Cellulose Industries.

Celluloses, fibrous material, used as such:

(1) *Mechanical* with *incidental chemical treatments* (bleaching, dyeing, mercerising finishing):
   Textiles, fine fabrics:
      Cotton, flax, hemp, ramie.
   Coarse textiles:
      Jute (flax and hemp).

Ropes, twines:
Hemp flax, manilla, aloe, and fibres of monocotyledons.
Hat-making materials:
Straw, wood.
Paper, boards, and fibrous agglomerates:
Cotton and linen rags and textile wastes (wood, straw, esparto pulps).

(2) *Chemical industries.* Cellulose derivatives, or celluloses, or products of resolution of compound celluloses.
Explosives:
Nitro celluloses.
Artificial fibres:
Nitro celluloses (acetates).
Aqueous solutions of cellulose derivatives.
Zinc chloride, cuprammonium, xanthogenic ester (viscose).
Films or sheets:
Nitrocellulose (acetates), xanthogenic ester.
Massive solids:
Nitrocellulose (acetates), xanthogenic esters.
Preparation of wood pulp, esparto, straw, and other celluloses for paper making:
Treatment of coniferous woods, esparto, straw, and textile waste materials.

(3) *Products of decomposition:*
Oxalic acid:
Fusion of wood wastes with alkaline hydroxides.
Acetic acid, wood spirit, acetone, creosote, charcoal:
Products of destructive distillation of woods.

Bibliography.

General.

'Cellulose,' Cross and Bevan, Longmans, London, 2nd ed. (1901). A text-book of the subject.

'Researches on Cellulose,' I. (1900), II. (1905), Cross and Bevan. A general account of later investigations and researches, to respective dates.

'Chemie der Zellulose,' by C. G. Schwalbe, Berlin, 1910. Full general account of contributions of original workers. Exhaustive bibliography.

'Die Zellulose,' by C. Piest, Stuttgart (1901), F. Enke. General account of subject, but with special reference to explosives.

'Cellulose, Cellulose Produckte,' 1st ed. Bersch, Leipzig (1904), Hartleben. A useful account of cellulose industries.

Special.

'Pflanzenfaser,' Hugo Müller. A. W. Hofman's Bericht, Entwicklung d. Chem. Ind. Braunschweig (Vienna Exhibition Reports, 1873). Original investigations of cellulose and fibrous materials. A pioneer technological study.

'Études sur les Fibres Vegetales,' Vetillart, Paris (1876). Miscroscopic study of structural characteristics of cellulose and fibres: a pioneer work.

'Text-book of Papermaking,' Cross and Bevan (Spon), 3rd ed. Principles of industrial preparation and application of cellulose, &c.

'Chemistry of Papermaking,' Griffin and Little, (New York) Lockwood. 'Die Cellulose Fabrication,' Max Schubert, Berlin, (1906) M. Krayn. Full account of wood pulp and processes of treatment.

'Die Mercerisation der Baumwolle,' P. Gardner, Berlin, (1878) Springer. A full account of mercerising process, and lustre finishes of textiles, with special reference to patent literature.

'Künstliche Seide,' Süvern, Berlin, Springer. A full account of artificial silk processes, with special reference to patent literature.

'Die Viskose,' B. M. Margösches, Leipzig (1906). An exhaustive account of scientific and technical papers, and patent literature of viscose developments. C.F.C.

CELTITE *v.* EXPLOSIVES.

CEMENT. In this article the word 'cement' is used to mean a calcareous compound employed in building, and does not refer to minor adhesives of the class typified by glue.

Portland cement. This material is so greatly more important than any other cement of its class, that it may appropriately be dealt with first. The name is trivial, referring merely to the colour of the set product which somewhat resembles that of Portland stone. The invention of Portland cement is attributed to Aspdin of Leeds, who calcined a mixture of chalk and clay, and found that the product, when ground and mixed with water, would set; but development from this elementary stage to the status of a valuable industry was the work of many minds, which, operating mostly empirically, arrived at a procedure competent to ensure a commercially useful product, although by methods of which the *rationale* was only dimly understood. At the present time, a better state of knowledge exists, and except in a few minor points, such as the adjustment of the setting time, which still cannot always be completely controlled, the manufacture is performed with precision and the product is of uniform and excellent quality. Nevertheless, the chemistry, both of the formation of Portland cement from its raw materials and of the changes which it undergoes on setting, is incomplete, many of the reactions supposed to occur remaining obscure and hypothetical.

Composition.—Portland cement consists of a mixture of compounds of lime and silica and of lime and alumina. These are the essential constituents, but it commonly contains in addition loose compounds of lime with ferric oxide, magnesia, and small quantities of inert insoluble silica or silicates, alkalis and sulphates. Except when perfectly calcined and absolutely fresh, it also contains a little water and carbonic anhydride absorbed from the air. The ultimate composition of Portland cement varies with the nature of the raw materials from which it has been made. The following is a typical analysis of cement made from chalk and clay in the Thames and Medway district:—

	Per cent.
Silica (SiO_2)	22·0
Insoluble silicious matter	1·0
Alumina (Al_2O_3)	7·5
Ferric oxide (Fe_2O_3)	3·5
Lime (CaO)	62·0
Magnesia (MgO)	1·0
Sulphuric anhydride (SO_3)	1·5
Carbonic anhydride (CO_2)	0·5
Water (H_2O)	0·5
Alkalis	0·5
	100·0

All the constituents may depart a good deal from these proportions. The silica may vary from 18 to 27 p.c., the alumina from 5 to 10 p.c., the ferric oxide from *nil* to 7 p.c., the lime from 58 to 67 p.c., the magnesia up to 3 p.c., the sulphuric anhydride up to 2·75 p.c., the alkalis to 2 p.c., and the water and carbonic anhydride according to the length of time the cement has been made and the extent to which it has been exposed.

The limits laid down by the British Standard specification are as follows: The proportion of lime to silica and alumina shall be not greater than the maximum nor less than the minimum ratio (calculated in chemical equivalents) represented by $\frac{CaO}{SiO_2 + Al_2O_3} = 2{\cdot}85$ or 2·0 respectively. The percentage of insoluble residue shall not exceed 1·5 p.c.; that of magnesia shall not exceed 3 p.c.; and the total sulphur content calculated as sulphuric anhydride (SO_3) shall not exceed 2·75 p.c. The total loss on ignition shall not exceed 2 p.c., unless it can be shown that the cement has been ground for more than four weeks.

Although the ultimate composition of Portland cement is easily and accurately ascertained by the ordinary methods of chemical analysis, its proximate composition, that is, the nature and quantity of the chemical compounds or physical mixtures which constitute it, are not known with exactness and cannot be determined with precision by existing methods of inquiry. Until recently, the view most in favour and best supported by experimental evidence, was that the essential constituent is tricalcium silicate $3CaO{\cdot}SiO_2$, and that the body next in importance is a calcium aluminate, to which the formula $2CaO{\cdot}Al_2O_3$, or alternatively $3CaO{\cdot}Al_2O_3$, is assigned. Dicalcium silicate $2CaO{\cdot}SiO_2$ is also present. The oxide of iron occurs as a calcium ferrite, the magnesia possibly as such, the sulphuric anhydride and carbonic anhydride probably as calcium sulphate and carbonate, and the alkalis perhaps as double compounds with lime and silica or alumina. As far as is known, the substances of primary importance are the tricalcium silicate and aluminate only, the minor bodies being little more than makeweights with the exception of calcium sulphate, which is of moment, because of its influence on the setting time of the cementitious constituents proper. The best proof that these smaller constituents are not essential is afforded by the fact that Portland cement of the highest quality can be prepared containing only silica, alumina, and lime in proper proportions.

The tricalcium silicate, the dicalcium silicate, and the tricalcium aluminate (or dicalcium aluminate), exist not separately but as solid solutions which are recognisable as distinct minerals in Portland cement clinker. The mineral termed *alite* is a solid solution of tri-(or di-)calcium aluminate in tricalcium silicate, whilst the solid solution of dicalcium aluminate in dicalcium silicate is called *celite*. As both are solid solutions and not definite compounds, their composition is not constant, but varies within the limits of solubility of the solute in each case. Celite appears to be almost inert, and to take little part in the setting of the cement, but alite is decomposed by water, and both the calcium silicate and calcium aluminate are hydrated according to the following equations, in which, for simplicity, the two substances are dealt with separately:—

(1) $2(3CaO{\cdot}SiO_2)+9H_2O=2(CaOSiO_2)5H_2O+4Ca(OH_2)$.
Tricalcium silicate. Hydrated monocalcium silicate.

(2) $3CaO{\cdot}Al_2O_3+12H_2O=3CaO{\cdot}Al_2O_312H_2O$.
Tricalcium aluminate. Hydrated tricalcium aluminate.

It will be seen that in the process of hydration of the tricalcium silicate, two-thirds of the lime are liberated and appear as calcium hydroxide, and in consequence this substance forms a large proportion of Portland cement when set; although—accepting the tricalcium silicate view—uncombined lime is absent from Portland cement as it comes from the kiln.

The belief that tricalcium silicate is the essential constituent of Portland cement has been disputed on the ground that there is no conclusive proof of the existence of this body as a definite chemical individual. The alternative theory is that the essential constituent is dicalcium silicate $2CaO{\cdot}SiO_2$, associated as a solid solution with lime, which may be present in amount equal to that occurring in the tricalcium compound. On this assumption, the equations written above would still stand with the modification that this part of the lime is hydrated directly on setting, instead of being both liberated and hydrated by the action of water. Whichever view may be nearer the truth, it is certain that set Portland cement contains large quantities of calcium hydroxide, a fact which has an important practical bearing in the use of the material, as will be shown when dealing with puzzuolana.

Manufacture.—As would be expected from what has been said concerning the composition of Portland cement, the raw materials from which it can be prepared are of the most varied description. Chalk, limestone, or any other approximately pure form of calcium carbonate on the one side, and clay, shale, or any typical argillaceous material on the other, can be mixed and burned together to produce Portland cement, provided that the product has a composition falling within the limits already laid down. It follows naturally that substances which contain both calcium carbonate and clayey matter, such as calcareous shales and argillaceous limestones, can be similarly used. On this account and because of the low price of the manufactured article and the consequent high proportion which freight bears to the total cost at the point of consumption, the manufacture of Portland cement is not confined to a particular spot, but is successfully undertaken wherever deposits of suitable raw materials occur, provided the cost

of fuel is not extravagantly high. But although it is perfectly practicable to manufacture Portland cement from a wide range of raw materials, yet certain of these possess qualities which give them a substantial advantage. The large deposits of chalk in the Thames and Medway district, together with the clay in the form of river mud adjacent thereto, make this region one of the centres of the industry in this country. In like manner, the existence of huge quantities of argillaceous limestone in Pennsylvania has led to the establishment of many large works in that State. In the former case, the chalk and clay, being soft materials, can be readily handled and intimately mixed, and in the latter the mingling of the calcareous and argillaceous ingredients has already been accomplished, and a correct composition can be attained by the addition of a small amount of pure limestone.

The following are analyses of some of the raw materials commonly employed:—

Chalk.

	Per cent.
Moisture	19·03
Sand and clay	0·93
Combined silica (SiO_2)	0·43
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	0·48
Lime (CaO) [1]	42·90
Magnesia (MgO)	0·42
Carbonic anhydride (CO_2)	34·16
Alkalis, organic matter, and loss	1·65
	100·00

Clay.

	Per cent.
Sand	28·42
Combined silica (SiO_2)	30·32
Alumina (Al_2O_3)	15·49
Ferric oxide (Fe_2O_3)	7·74
Lime (CaO)	2·04
Magnesia (MgO)	1·96
Sulphuric anhydride (SO_3)	1·96
Combined water and loss	12·07
	100·00

Limestone.

	Per cent.
Insoluble silicious matter	0·20
Alumina+ferric oxide ($Al_2O_3+Fe_2O_3$)	0·08
Lime (CaO)	56·02
Magnesia (MgO)	0·24
Carbonic anhydride (CO_2) [2]	43·38
Combined water and loss	0·18
	100·10

Shale.

	Per cent.
Silica (SiO_2)	60·22
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	27·20
Lime (CaO)	trace
Magnesia (MgO)	1·62
Carbonic anhydride+water (CO_2+H_2O)	4·54
Alkalis and loss	6·42
	100·00

[1] Corresponding with calcium carbonate ($CaCO_3$) 76·60 p.c.

[2] Corresponding with calcium carbonate ($CaCO_3$) 98·36 p.c.

Marl.

	Per cent.
Silica (SiO_2)	15·10
Ferric oxide+alumina ($Fe_2O_3+Al_2O_3$)	7·30
Lime (CaO)	42·16
Magnesia (MgO)	0·34
Carbonic anhydride (CO_2)	33·51
Water, alkalis, and loss	1·59
	100·00

Whatever may be the raw materials, the first step in the manufacture of Portland cement is to secure their comminution and intimate admixture. It must be understood that as the process of burning cement involves the sintering but not the fusion of the materials, these two conditions are of primary importance. The raw materials are commonly ground so that they leave a residue of less than 10 p.c. on a 180 × 180-mesh sieve, and intimacy of contact is secured by mixing the materials together at as early a stage of the process of comminution as is practicable, and in addition grinding them together.

The procedure is as follows: In the case of soft, wet raw materials, such as chalk and clay, the two substances in proportions determined from their analysis are weighed into a wash mill, which is a large tank in which a vertical spindle having radial arms from which depend harrows is caused to revolve. Enough water is added to allow the materials, when well beaten up, to form a thick cream or slurry, which is mobile enough to flow and to be pumped. The slurry passes through screens to retain stones and grit, and is ground either between millstones or in more modern practice in a tube mill, which is a cylinder made of steel lined with a hard material such as quartzite blocks and partly filled with flint pebbles. The cylinder is set horizontally and revolved, the slurry being fed in through a trunnion and passing out at the other end. During its passage through the cylinder, it is ground by the pebbles which are continually raised up the periphery of the cylinder and continually drop back through the liquid mass, pounding its particles on the lining of the cylinder and between the pebbles themselves. After being thus ground, the slurry flows into large reservoirs, called dosage tanks, where it is sampled and analysed and, if necessary, its composition is corrected by the addition of more chalk or clay. In the early days of the industry, the slurry was prepared with so large a proportion of water as to be a thin cream from which the water was allowed to settle in large tanks, the supernatant water being drawn off and the deposited solids dug out when they had arrived at the consistency of mud, and this method is still occasionally practised. Usually, however, the quantity of water used is the least that will allow the slurry to flow (35 to 50 p.c. of the weight of the slurry, according to the nature of the raw materials), adequate mixture being thus obtained and the delay and cost of double handling avoided. The next step is to dry and burn the slurry to clinker. The modern method combines these operations, the slurry being pumped into the upper end of a rotatory kiln (*see* below), where it is dried and burned as it travels down the kiln. Before the invention of the rotatory kiln, drying was effected either by the heat of coke ovens used for manufacturing the coke

needed in the subsequent burning or by the waste heat of chamber kilns (*see* below), the mass thus dried cracking into rough cakes suitable for loading into the kiln. Where the kiln was of a type which provided no surplus heat, the slurry was dried independently, crushed, and moistened with a little fresh slurry, moulded into bricks, redried and burnt. The choice among these various procedures depends on the kind of kiln for which the slurry is destined.

When dry raw materials such as limestone and shale are used, they are crushed in a stone breaker or between rollers, according to their hardness, any moisture such as quarry water or damp from exposure to weather being removed by passing through rotating cylinders, heated by flue gases, or by an independent fire or in towers through which hot air is blown, and are ground together in the calculated proportions. The grinding is performed by ball mills, consisting of a drum lined with perforated steel plates and partly filled with steel balls, followed by a tube mill, such as has been described above, or in mills of the Huntingdon class, in which rollers depending from spindles attached to a vertical axle are driven outwards by centrifugal force as the spindle is rotated and bear against a steel grinding ring between which and the rollers the material is ground. It will be understood that many different forms of comminuting apparatus can be and are used in cement works, according to the nature of the material. Discussion of their relative merits would be out of place in an article of this kind. The dry raw materials are fed as powder (often slightly damped to prevent dust) direct into a rotatory kiln or are moistened sufficiently to allow them to be moulded into bricks, dried and burnt in one of the kinds of fixed kiln.

Although wet raw materials are naturally ground wet, and dry raw materials are ground dry, yet occasionally dry raw materials are ground wet, it being maintained by some that any extra expenditure of heat to drive off the water added is compensated for by the more intimate admixture of the raw materials and the ease with which the slurry may be conveyed by being pumped or allowed to flow in contrast to dry raw materials which require elevators, worm conveyors and similar mechanism.

The raw materials finely ground, intimately mixed and in correct proportion (containing in most cases about 75 p.c. of calcium carbonate calculated on the dry substance, the balance being the clayey constituents) are burnt to cement clinker in various types of kiln.

The earliest was the bottle kiln, a dome-shaped brick structure lined with fire bricks, having a short chimney and a grate. The lumps of dried slurry were loaded into this, mixed with coke, and the charge fired and allowed to burn out, the products of combustion escaping at the top of the kiln. An improvement on this is the chamber kiln shown in Fig. 1. It is a cup-shaped structure, lined with fire brick, in which the dried slurry and coke are placed in layers, communicating with a wide flue, which forms a floor on to which wet slurry can be run, the far end of the flue being connected with a chimney stack. The hot gases from the kiln proper pass over the slurry and dry it, so that a charge is ready when the previous one is burnt. An ordinary chamber kiln will produce about 30 tons of clinker per run, which, including loading and discharging, usually takes a week, and it will burn 40–50 p.c. of coke, reckoned on the weight of clinker produced. The coke is generally bought from gas works, though formerly coke ovens were in use at the cement works themselves, the products other than coke being wasted. As the coke and raw materials are mixed in the kiln, the ash of the coke appears

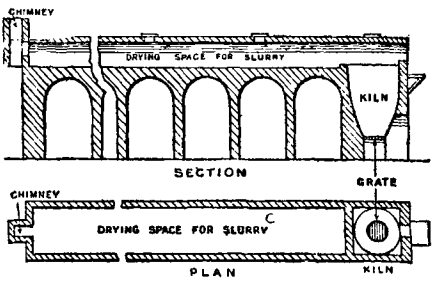


FIG. 1.—CHAMBER KILN.

in the finished cement, raising the proportion of silica appreciably; on this account it is customary to use raw materials containing a higher percentage of calcium carbonate in a kiln of this kind than in one in which the whole of the ash is not retained, so as to compensate for the added silicious matter, but even with this precaution the product is irregular, the ash attaching itself chiefly to the outside of the clinker and not penetrating to the centre of the lumps. It is impracticable to burn the material uniformly. Parts will be almost fused, parts merely lightly calcined and decarbonated, barely sintered and not truly clinkered, while yet other parts will have attacked the silicious lining of the kiln, forming with it a sort of slag. Hence it is necessary to pick the charge when it is drawn, rejecting the underburnt and the slagged material, and on the perfection of this picking the quality of the finished cement largely depends.

The shaft kiln is another type of fixed kiln in which the fuel is mixed with the raw material. There are various forms of shaft kiln, but the principle is the same in all cases, the raw material and fuel proceeding vertically down a shaft to a point where combustion occurs, and passing from this down a continuation of the shaft to a drawing hole from which the clinker can be extracted. Loading and drawing proceed regularly, the kiln working continuously instead of intermittently, as does the chamber kiln. The working is regenerative in the sense that the products of combustion from the burning zone pass up through the unburnt raw material, which is thereby heated and the air for combustion flows through the hot clinker in the lower part of the kiln, and thus is heated before taking part in the combustion. The Schneider and the Aalborg kiln are examples of this type, the latter is shown in Fig. 2. Another well-known shaft kiln with the modification that the upper and lower parts of the shaft are not in the same vertical line, is the Dietsch kiln (Fig. 3). In this, the heated raw material is received on a stage

between the upper and lower part of the shaft, and passes thence into the burning zone. In the illustration, two such kilns are shown, built back to back. There are various modifications of the shaft kiln differing in details of design, some working with forced draught. From their regenerative mode of working, they are economical of fuel, but require a good deal of moderately skilled labour and give a product mixed with the ash of the fuel and requiring picking.

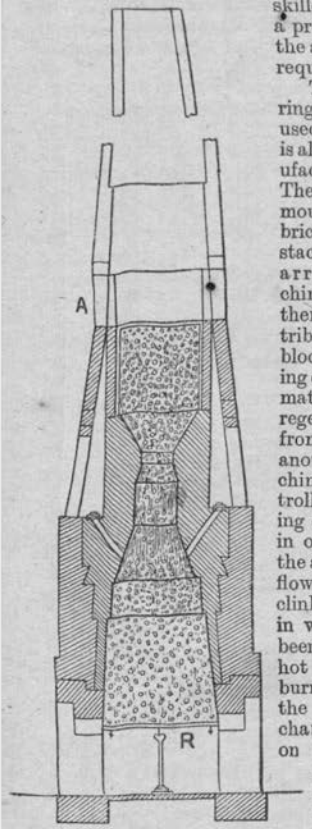


FIG. 2.—AALBORG KILN.

The Hoffmann or ring kiln (Fig. 4), largely used for brick making, is also used in the manufacture of cement. The materials are moulded into rough bricks, and these are stacked in chambers arranged round a chimney which serves them all. Fuel is distributed between the blocks, and the working of the kiln is systematic, continuous, and regenerative. Passage from one chamber to another and to the chimney can be controlled, and thus burning can be carried on in one chamber while the air for combustion flows in through hot clinker in chambers in which burning has been finished and the hot gases from the burning chamber heat the raw material in chambers ahead of it on their way to the chimney, the chamber representing the locus of combination continually shifting forward step by step all round the ring. As might be expected, this kiln is economical of fuel, but costly in labour for loading and unloading the chambers, and yields a product lacking uniformity.

In modern practice, these various kinds of fixed kiln have been displaced by the rotatory kiln, which, though originating in this country some 30 years ago, was brought to a working success in the United States, and began to be adopted here and on the Continent about 1898. This kiln is a steel cylinder lined with fire brick, set at a small angle with the horizontal, and capable of being slowly rotated round its axis. At the upper end the raw material is fed in, and at the lower is a burner sufficiently powerful to reach a clinkering temperature (about 1400° C.). As the cylinder rotates, the raw material travels down the cylinder on account of the inclination, and on its journey is gradually raised in temperature until it reaches the lower end, where it is clinkered and drops out. The process is continuous, systematic, and to a considerable extent regenerative. The labour required is small and the output large per unit of plant. A large proportion of the fuel ash passes through the kiln without attaching itself to the raw material, and such portion as remains is incorporated with the raw materials and forms part of the finished product instead of being largely confined to the surface of the clinker. When burning is carried out properly, the whole of the product is uniformly clinkered and needs no picking.

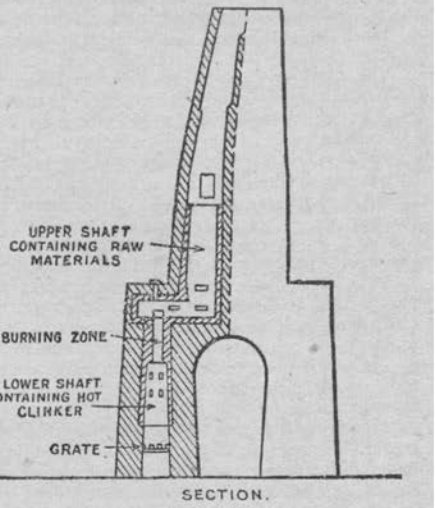


FIG. 3.—DIETSCH KILN.

The earlier rotatory kilns were some 60 feet long and 6 feet external diameter. At the present time, an ordinary size is 150 × 8 feet and larger have been made and used. The output of a single kiln is 200 to 800 tons a week, according to its size, as compared with 30 to 70 tons a week for a fixed kiln. A rotatory kiln is run as nearly as possible day and night, including Sundays, throughout the year, stoppages being made only for repairs or to patch the

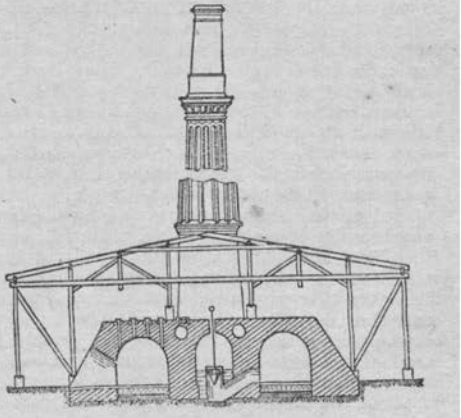


FIG. 4—HOFFMAN KILN.

coating of clinker which forms on the fire-brick lining of the kiln (Fig. 5). The kiln is commonly cylindrical, but some designs are of larger diameter at the burning end, so as to provide a wider portion at the place where combustion is at its height. The earliest form of rotatory kiln which approached success, was fired with producer gas, but many difficulties arose in the use of this fuel, and although the idea has merits and has been revived, it has not reached fruition. Oil burners, like a large blast lamp, having the oil sprayed in by steam or compressed air, are used with complete success wherever oil is cheap enough, but as the cost is too high in most countries, powdered coal is the standard fuel. Coal, preferably bituminous, and containing a moderate amount (10 p.c.) of ash when well dried and very finely powdered, can be used to form a sort of blowpipe flame much as if it were a fluid, the powder being driven into the kiln by a blast of air and issuing from a jet much as gas might do, and burning there in a supply of secondary air supplied to the space around the jet and preferably pre-heated. In actual working, these conditions are realised in the following way: Small coal is dried in a rotatory drier heated by an independent fire or by the kiln gases. It is powdered very finely so as to leave not more than 5 p.c. residue on a sieve having 180×180 meshes per square inch. This powdered fuel is fed from a hopper into a pipe through which air is being driven by an air compressor or a fan, and issues from the mouth of this pipe, which passes through a shield or screen covering the lower end of the kiln, as a jet of dry finely powdered combustible matter carried by a blast of air, insufficient for its combustion and serving chiefly as a means for its propulsion in the form of a jet. This jet is set into the mouth of the kiln and pointing towards the far end. Air for the combustion is drawn in by the draught of the chimney stack, with which the upper end of the kiln communicates, and on its way passes through a rotating cylinder down which is proceeding the red-hot clinker issuing from the kiln, absorbing a portion of that heat, and carrying it to the place of combustion. By these means a powerful jet of flame is produced, the temperature of which is ample for clinkering.

Either dry or wet raw materials can be burned in a rotatory kiln. Dry materials are fed in by a screw, the mass being usually slightly damped by a small proportion of water in the trough in which the screw works, so that the

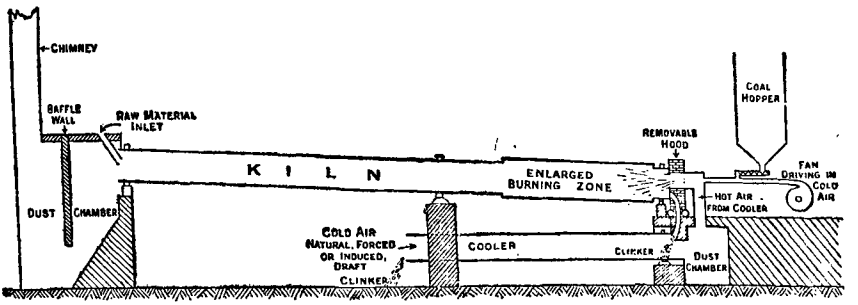


FIG. 5.

fine dusty particles are not carried away by the draught of the kiln. Wet raw materials are simply allowed to flow in from a trough in which the height of the slurry is maintained constant by a device such as a pump more than capable of the maximum flow, the surplus being returned by a by-pass. The water, about 40 p.c. of the weight of the slurry, is evaporated by the hot gases coming from the lower end of the kiln, and the dried slurry forms itself into small nut-like masses as it rolls round the inside of the cylinder. These travel slowly downwards in a spiral path, and their temperature rises until the calcium carbonate is decomposed, the clay is dehydrated, and union begins between the acid and basic oxides, the silica, alumina, and ferric oxide acting in the first and the lime, magnesia and alkalis in the second sense, until finally the material becomes slightly plastic, and full combination is effected at a point near the lower end of the kiln, where the temperature is highest. The white-hot clinker passes into a cooler, such as the rotating inclined cylinder already mentioned in connection with the heating of the air necessary for combustion, where it is often sprinkled with water for the double purpose of completing its cooling and of hydrating any lime which may not have been perfectly combined in the kiln.

With dry raw materials the course of operations is the same, save that only the small quantity of water used to prevent dust has to be evaporated.

On account of the fact that cement clinker is a basic material and that fire brick is an acid substance, using those words in the ordinary metallurgical sense, interaction may occur between these at a clinkering temperature, and a slag may be produced. Any overheating will cause the rapid formation of this slag, with the result that the clinker will be spoiled and the lining destroyed. But if the burning is properly conducted, the action is not uncontrollable, and further can be prevented by the device of beating down the slightly plastic clinker on to the fire-brick lining, so that it adheres and itself forms the true lining, to which, of course, the rest of the clinker is chemically indifferent. The coating breaks away from time to time, and needs to be patched by beating down fresh clinker on the fire brick thus left bare. Linings of less acid substances such as bauxite, and basic linings such as magnesia bricks, have been tried, but all present some practical defect which makes them less suitable than fire brick used in the way described.

Good well-burnt clinker, whether made in a

fixed or a rotatory kiln, is a hard rock-like mass of dark colour, varying from brown to almost black. The pieces of clinker from fixed kilns are chiefly rough lumps of similar size to that of the blocks of raw material, and need a preliminary crushing in a stone breaker before they can be ground. The product from a rotatory kiln is in the form of small rounded masses, varying in size from a pea to a walnut. Sometimes a number of these will stick together, making a mass a foot or more in diameter, but the bulk of the product is small enough to be ground without previous crushing.

Grinding is effected in machines similar to those used for preparing the raw materials. Ball and tube mills and mills of the Griffin and Huntingdon class are in most general use, millstones, such as were used for grinding corn, having been superseded on account of their small output and heavy upkeep. The clinker is ground to cement having a residue of not more than 18 p.c. on a 180 × 180-mesh sieve, and is conveyed mechanically to warehouses where it is stored and bagged or filled into casks. In a modern works, the whole operation from the reception of the raw materials to the filling of the bags is conducted almost wholly mechanically, manual labour being eliminated as completely as possible, an object easily attained with rotatory kilns, which do not require to be loaded and unloaded by hand.

Testing Portland cement. The quality of Portland cement and its suitability for building purposes is ascertained by various mechanical tests and by its chemical analysis. The analysis shows whether the constituents fall within the recognised limits stated above, and detects the presence of such adulterants as blast furnace slag or Kentish rag (a silicious limestone), which differ widely from cement in composition or contain some characteristic constituent such as calcium sulphide, which is almost or wholly absent from Portland cement. But as it is impracticable to make a *proximate* analysis of Portland cement, the ordinary analytical figures will not indicate whether the raw materials have been sufficiently intimately mixed and sufficiently thoroughly burnt to form those cementitious substances constituting sound and serviceable Portland cement. This question can, however, be satisfactorily settled by physical and mechanical tests. The specific gravity of the cement is a useful criterion, as, if below the normal value (say 3·15), it may generally be inferred that the cement has been underburnt. The mechanical strength of the cement by itself and when made into a mortar with sand can be determined. The fineness to which the cement has been ground is a useful indication of quality, inasmuch as the coarser parts hydrate so slowly as to be of little or no cementitious value. The time of setting is useful in aiding choice of a cement for a given class of work. Finally, the soundness of cement, that is, its constancy of volume when set and consequent freedom from tendency to expand in the work of which it forms part, and thus to subject the work to internal stresses sometimes so great as to cause its destruction, can be determined by observing the alteration of volume and condition of test pieces made of the cement and kept under conditions designed to develop and accelerate any latent tendency of the kind. Codes of testing, covering this point, are in common use in all countries, and as an example the clauses relating to testing may be quoted from the British Standard specification for Portland cement:—

'*Test for Soundness.*'

'The cement shall be tested by the Le Chatelier method.

'The apparatus for conducting the Le Chatelier test is to consist of a small split cylinder of spring brass or other suitable metal of 0·5 mm. (0·0197 inch) in thickness, forming a mould 30 mm. ($1\frac{3}{16}$ inches) internal diameter and 30 mm. high. On either side of the split are attached two indicators with pointed ends, the distance from these ends to the centre of the cylinder being 165 mm. ($6\frac{1}{2}$ inches).

'In conducting the test, the mould is to be placed upon a small piece of glass and filled with cement gauged in the mode and under the conditions referred to in section (*d*) of clause 7, care being taken to keep the edges of the mould gently together whilst this operation is being performed. The mould is then to be covered with another glass plate, a small weight is to be placed on this, and the mould is then to be immediately placed in water at a temperature of 58° to 64°F. and left there for 24 hours.

'The distance separating the indicator points is then to be measured, and the mould again placed in water at 58° to 64°F., which is to be brought to boiling-point in 25 to 30 minutes and kept boiling for 6 hours. After removing the mould from the water and allowing it to cool, the distance between the points is again to be measured; the difference between the two measurements represents the expansion of the cement, and must not exceed the following limits, viz.: 10 mm. when the sample has been aërated for 24 hours in the manner hereinbefore described; or, if the above test has failed, 5 mm. after the sample has been aërated for 7 days in the same manner.'

The specifications in use on the Continent and in America are similar to the British Standard specification as regards their aim, which is to ensure that the cement shall be mechanically strong and chemically stable. The tests themselves are also generally similar, the chief differences concerning the use of compressive as well as tensile tests and variations in the mode of determining the soundness of the cement.

Other cements of the Portland class. Roughly it may be said that all cements made by burning a mixture of calcareous and argillaceous materials are of the Portland cement class, although they may not be true Portland cement. Roman cement is an example. It was manufactured before the invention of Portland cement by calcining the nodules of indurated chalk and clay called *septaria*, and dredged upon the Kent and Essex coasts. On burning, without any preparation, these nodules give a cement having a composition of which the following analysis is an example:—

	Per cent
Silica (SiO_2)	19·62
Insoluble residue	5·86
Alumina (Al_2O_3)	10·30
Ferric oxide (Fe_2O_3)	7·44
Manganese oxide (MnO)	1·57
Lime (CaO)	44·54

	Per cent.
Magnesia (MgO)	2·92
Sulphuric anhydride (SO_3)	2·61
Carbonic anhydride (CO_2)	3·43
Water (H_2O)	0·25
Alkalis and loss	1·46
	100·00

Roman cement has been almost wholly replaced by Portland cement. It is reddish in colour and very quick-setting, this property making it useful for work which has to be exposed to water immediately after it is laid.

Various marls contain chalk and clay in about the proportion necessary to constitute Portland cement. These are burnt without preparation and form what is known as 'natural cement.' Cement of this sort is, of course, irregular in composition and is apt to be unsound. If well slaked before use, it is a serviceable material of its class. Magnesian limestones containing argillaceous matter, are largely used in the United States for making natural cement. The following is an example of their composition :—

	Per cent.
Silica (SiO_2)	22·77
Alumina+Ferric oxide (Al_2O_3+Fe_2O_3)	10·43
Lime (CaO)	34·54
Magnesia (MgO)	21·85
Sulphuric anhydride (SO_3)	1·44
Carbonic anhydride (CO_2)	2·84
Alkalis	3·63
Water and loss	2·50
	100·00

Hydraulic limes are cements of the Portland class, and are made by burning limestones containing sufficient clayey matter to yield the calcium silicates and aluminates necessary in hydraulic cement. There are two types, with many gradations between them. The first is Chaux de Teil, made by burning a limestone containing silica so finely divided and so evenly distributed that it unites almost completely with the lime without the aid of any considerable quantity of fluxing constituents, such as alumina and oxide of iron. Its composition is shown below :

	Per cent.
Insoluble residue	0·62
Silica (SiO_2)	22·10
Alumina (Al_2O_3) + Ferric oxide (Fe_2O_3)	1·82
Lime (CaO)	66·72
Magnesia (MgO)	1·17
Sulphuric anhydride (SO_3)	0·49
Carbonic anhydride	0·64
Water (H_2O)	5·36
Alkalis and loss	1·08
	100·00

The second instance is afforded by the hydraulic lime prepared from blue lias limestone occurring in the Rugby district, near Lyme Regis and by Aberthaw. In this material, the proportion of alumina is much higher relatively to the silica than in the case of the Chaux de Teil. An example of its composition is appended ;

	Per cent.
Insoluble residue	2·39
Combined silica (SiO_2)	14·17
Alumina (Al_2O_3)	6·79
Ferric oxide (Fe_2O_3)	2·34
Lime (CaO)	63·43
Magnesia (MgO)	1·54
Sulphuric anhydride (SO_3)	1·63
Carbonic anhydride (CO_2)	3·64
Water (H_2O)	2·69
Alkalis and loss	1·38
	100·00

As it is not designed in the case of hydraulic limes to cause complete union of the acid and basic oxides, they invariably contain free lime which needs to be slaked. This is done systematically by the manufacturer of lime of the Chaux de Teil class, but is not generally practised in this country, the operation being performed by the user. In either case, perfect slaking is necessary because any negligence in this respect will lead to expansion in the work of which the lime forms part, and the slaking must be accomplished in such a way that, whilst the free lime is slaked, the cementitious compounds remain untouched.

Cements made from blast-furnace slag. Blast-furnace slag granulated by being run into water is feebly hydraulic if its lime content is sufficiently high. It is used as a puzzuolana (*see* below). If the slag is mixed with limestone so as to bring its composition within the limits indicated for Portland cement, and the mixture is burnt, a product is obtained which is as much Portland cement as if it had been made from chalk and clay. There is, however, a material made in Germany and known as Eisen-Portland cement, which consists of Portland cement (often made from blast furnace slag) to which some 25 p.c. of slag has been added after the manufacture of the Portland cement itself. The slag added has a puzzuolanic function similar to that of other silicious materials which are sometimes added to Portland cement. But apart from these uses of slag, various patented products, of which Passow cement and Collos cement are examples, prepared by treating liquid blast furnace slag in such a way that it becomes definitely hydraulic and will set and resist the action of water as does Portland cement, are manufactured. Processes for making these cements generally consist in suddenly cooling the liquid slag and in adding to it, at the moment of cooling, small quantities of some extraneous material such as salts of magnesium or the alkalis. The cause of the action of the mode of cooling and of the addition is obscure, but the fact remains that in this manner blast-furnace slag, which untreated is relatively inert, is converted into a true hydraulic cement.

Puzzuolanic cements. Except for limes which being made from a silicious limestone, happened to possess hydraulic properties, the earliest kind of hydraulic cement was made from ordinary lime mixed with a puzzuolana, that is, a silicious material sufficiently active to combine with the lime and form a cementitious silicate. Natural puzzuolanas are volcanic in origin, the deposits known as Roman and Neapolitan puzzuolana, santorin earth, and trass being examples.

Analyses are given below of Roman and

Neapolitan puzzuolanas and of a similar material from Java :

—	Neapolitan puzzuolana	Roman puzzuolana	Java trass
	p.c.	p.c.	p.c.
Insoluble siliceous matter	35·38	25·94	50·40
Soluble silica (SiO_2)	27·80	32·64	19·32
Alumina + Ferric oxide ($Al_2O_3 + Fe_2O_3$)	19·80	22·74	16·96
Lime (CaO)	5·68	4·06	nil
Magnesia (MgO)	0·35	1·37	0·13
Sulphuric anhydride (SO_3)	trace	trace	—
Water + carbonic anhydride ($H_2O + CO_2$)	4·27	8·92	7·57
Moisture, alkalis, loss	6·72	4·33	5·62
	100·00	100·00	100·00

Granulated blast-furnace slag, broken brick and burnt clay are artificial puzzuolanas sometimes used to produce hydraulic cements when added to ordinary lime. The quantity to be added can be calculated on the assumption that the liberated lime combines in about the same proportion with the active silica in these as it does with the silica in Portland cement, it being understood that the siliceous material is sufficiently finely ground to unite with the lime. In practice, puzzuolanic materials are usually coarsely ground, and only a fraction of the active silica enters into combination, the balance of the puzzuolana acting merely as an aggregate.

From what has been said concerning the constitution of Portland cement and the formation of slaked lime by its hydration in setting, it will be seen that there is a considerable quantity of calcium hydroxide unprovided for by any acid oxide. It follows that this will act in the same way as ordinary slaked lime in combining with any active siliceous substance, and hence that puzzuolanas can be employed as additions to Portland cement which are useful in increasing its content of cementitious matter.

Use of Portland cement. The original object of manufacturing Portland cement and similar substances was to obtain a material which would both set and would resist the action of water. But it was soon found that the great mechanical strength of Portland cement made its use advantageous, even when it had not to be exposed to water, and at the present day it is the structural cement *par excellence*, and on account of the great decrease in cost due to modern method of manufacture, it tends to displace all other building cements, including common lime. Its largest application is to form concrete by cementing together any cheap inert stony material which may be locally available, and by the use of this substance, huge works of all kinds are constructed at a cost much inferior to that of the same work in masonry. It has been found that Portland cement, when made into mortar or concrete, will adhere strongly to iron and steel if the latter is clean and not too smooth, and on this observation the preparation of the material known as reinforced concrete is based. It is made by constructing a skeleton of mild steel rods, often tied together by steel wire and filled in with Portland cement concrete, the steel being so disposed as to take the tensile stresses in the composite structure. It fortunately happens that the coefficients of expansion by heat of ordinary mild steel and of concrete are nearly identical, and thus internal stresses, such as might occur where two diverse materials are bonded together and exposed to fluctuations of temperature, are of very moderate magnitude and do not appreciably influence the mechanical stability of the product. Although on the whole a permanent material, Portland cement may be injured or destroyed under various conditions incidental to its use. Set cement is the product of the action of water, but it is not indifferent to the further action of water. The products of the hydration of Portland cement and its congeners are calcium hydroxide, which is soluble in, and hydrated calcium silicates and aluminates which are decomposable by, water. Therefore when water has free access to set cement and can flow through the concrete or mortar of which it forms part, the cement is dissolved and destroyed. In practice good concrete is made so nearly impermeable that, except under heavy pressure, no such flow occurs, but if the concrete is loose in texture and the flow of water correspondingly easy, destruction is only a matter of time. When the water contains salts of magnesium or calcium sulphate, which act on the lime in the one case and on the calcium aluminate in the other, forming part of the set cement, the rate of destruction is much increased. Thus it comes about that in all under-water work, and more particularly in sea water, the concrete to be permanent must be impervious. There are minor and local causes of destruction such as contact with waters containing dissolved gases, *e.g.* CO_2 and SO_3, competent to act on the calcareous constituents of cement, but in general the failure of a concrete structure, when due to chemical action and not to mechanical weakness, can be traced to the flow of water, and usually saline water, through the fabric. B. B.

CEMENTATION *v.* IRON.

CEMENT COPPER *v.* COPPER.

CEMENT STEEL *v.* IRON.

CEMENTITE, an iron carbide, Fe_3C, containing 6·9 p.c. carbon, is an important constituent of cast iron and steel (Abel and Deering, Proc. Inst. Mech. Engineers, 1885, 30; Moissan, Compt. rend. 122, 421). In steels containing 1·5 p.c. or more of carbon, free cementite is found crystallised in large pseudo-hexagonal plates (Groth, Chem. Krystallographie, 1906, i.), and in practically all steels it exists with pure iron (*ferrite*), in the eutectic mixture called *pearlite* (Ledebur, Stahl u. Eisen, 1898, 742).

It is very brittle and harder than hardened steel or glass (H.=6) (Müller, Stahl u. Eisen, 1898, 292), and its presence is the cause of the hardness of 'white' or 'chilled' cast iron. (Howe, Metallographist, 1901, 177). It is recognised under the microscope by its hardness and resistance to etching.

As *cohenite*, it is present in meteorites (Weinschenck, Ann. Museum, Wien, 1889, 4, 94).

CERADIA *v.* OLEO-RESINS.

CERARGYRITE or **Hornsilver.** Native silver haloids, Ag(Cl,Br,I), occurring as small holohedral-cubic crystals and as compact masses with a horny appearance and texture. The material is soft (H.=2½), tough, and sectile, and

cuts like horn. On exposure to light, it quickly darkens. The name 'hornsilber' was used by C. Gesner in 1565, and the Greek form cerargyrite was first used by F. S. Beudant in 1832. After the recognition of the bromide and chlorobromide in 1841 and 1842, the name cerargyrite came to be applied more especially to the chloride. But as the different members of the group so closely resemble one another that they can often only be distinguished by analysis, it is more expedient to include them under the name cerargyrite as sub-species, viz.:

Chlorargyrite, AgCl.	Grey or colourless, sp.gr. 5·556.
Bromargyrite, AgBr.	Greenish-grey.
Embolite, Ag(Cl,Br).	Greenish-grey.
Iodembolite, Ag(Cl,Br,I).	Greenish-yellow to orange-yellow.

Isomorphous mixtures are the rule, and of these sub-species embolite (*q.v.*), with chlorine and bromine in indefinite proportions, is the most abundant. Large quantities of these minerals have been mined as silver ores in Mexico, Chañarcillo in Chile, and Broken Hill in New South Wales. They occur in the upper oxidised zones of veins of silver ore, and have no doubt been formed by the action of salt waters percolating from above (*see* Prior and Spencer, Mineralog. Mag. 1902, xiii. 174).

L. J. S.

CERASIN *v.* GUMS.

CERASINE, -ORANGE, -RED, *v.* AZO-COLOURING MATTERS.

CEREALS. The cereals are the fruits or seeds of various species of Gramineæ. In all parts of the world they constitute the most important food of mankind, and are utilised not only for bread corn and the feeding of stock, but also for the fabrication of a number of fermented drinks and industrial products like starch.

The most widely distributed cereals are wheat and barley, which grow in almost all climates; oats are more confined to northern latitudes; maize, and still more so rice, do not ripen, as a rule, north of 45°; while the millets, sorghum, and durra are truly tropical or subtropical in their habits.

In view of their importance as food, a very large number of analyses have been made of the various cereals grown under all conditions, and of the products manufactured from them; the most complete sources of information on this point are König, Chemie der menschlichen Nahr- und Genussm. 1903, and the various publications of the U. S. Dep. of Agric., Div. of Chemistry, particularly Bull. 13 (1899), 9, 45, and 50.

While each cereal grain possesses its own characteristic composition, subject to variations determined by climate, season, variety, &c., they have still a general similarity and possess many features in common. The predominant constituent is always starch, which, together with certain closely allied carbohydrates—the amylans—and a little sugar, forms from 50 to 80 p.c. of the whole grain. Various proteins are also present in inverse ratio to the carbohydrates; they fall as low as 6 p.c. in rice, and rise to 20 p.c. in some varieties of wheat. A small quantity of fat or oil is also found, most abundantly in maize and oats, where the average percentage is about 5–6. The proportion of fibre and of ash varies very greatly according to whether the grain of commerce consists of the naked fruit alone, as in wheat, rye, and maize, or whether, as in barley and oats, the flowering glumes remain adherent and can only be removed by subsequent manufacturing processes. The ash of the cereal grains shows certain marked characteristics: it is always very rich in phosphoric acid, up to nearly one-half of the ash when the grain is naked; potash and magnesia predominate among the bases, lime and soda being present in but small amounts, while still less chlorine or sulphuric acid (derived from organic sulphur compounds) are to be found; silica is almost absent from the naked grains, but may constitute 5–20 p.c. of the ash of these grains possessing an adherent husk.

The structure of all cereal grains shows the following features in common: in addition to the chaffy membranes of the flower, which may or may not be adherent, the grain proper possesses several fibrous coats or skins. Within these skins at the end of the grain formerly attached to the plant, lies the embryo or germ, constituting about 3 p.c. of the whole, but the greater part of the seed is occupied by the starchy endosperm, the outer membrane of the embryo which abuts against the endosperm being known as the scutellum. The endosperm consists of a series of thin walled cells tightly packed with starch grains enclosed within a thin network of protein, but immediately below the skin there exists a row of differently shaped cells known as the aleurone layer, especially rich in protein. It will now be convenient to consider the cereals separately.

Wheat. The average composition of wheat from various sources is given in Table I., extracted from the sources above quoted. A number of other analyses may also be found in Vilmorin, Bull. Soc. Nat. Agr. France, 1901, 61, 73.

The composition of wheat is subject to considerable variation, and as the value of the wheat for bread-making is intimately connected with the amount of nitrogen it contains, the effect of external conditions upon this constituent has been extensively studied. As factors bringing about variation, we may enumerate (1) variety, (2) climate, (3) season, (4) soil, (5) manuring, (6) date of cutting, &c.

(1) High nitrogen content in wheat is usually associated with a horny translucent grain, hardness, and strength (*i.e.* capacity to make a large well-piled loaf). These qualities are most markedly seen in the wheats from Manitoba, Kansas, Hungary, and South Russia, where the high nitrogen content is mainly due to environment but partly to the varieties grown. In England, where the climate tends to produce a soft, starchy wheat, it is found that variety is the chief factor in determining the proportion of nitrogen. In the typical English wheats, the variations in the percentage of nitrogen are small, 1·6 to 2·5 p.c., according to the season, but certain wheats, like Rough Chaff, Red Lammas and Golden Drop, always show higher percentages of nitrogen than others like Rivett, Square Head's Master, and Stand Up, when grown alongside on the same soil and in the same season. Moreover, a few varieties have been found, notably Fife, a wheat of Galician origin

TABLE I.—ANALYSES OF WHEAT.

—	No. of samples	Water	Protein	Fat	Carbo-hydrates	Crude fibre	Ash
English	22	13·37	10·99	1·86	69·21	2·90	1·67
United States	168	10·62	12·23	1·77	71·18	2·36	1·82
„ „ New York	8	10·38	12·34	1·92	71·63	2·07	1·67
„ „ Oregon	11	11·53	9·19	1·72	73·61	2·25	1·69
„ „ South Dakota	8	9·02	14·89	2·04	69·89	2·49	1·70
Canadian North-West (Fife)	18	12·05	13·84	1·79	68·53	2·21	1·58
France	70	15·20	12·64	1·41	68·92	2·00	1·66
Germany, S. and S.-W. winter wheat	52	13·37	12·29	1·71	67·96	2·82	1·85
„ „ spring „	30	13·37	14·95	1·56	67·93		2·19
Russian, spring wheat	39	13·37	17·65	1·58	65·74	—	1·66
Argentine	5	9·55	12·78	1·84	71·15	2·69	1·99
American—durum	2	10·40	15·68	2·49	76·74	2·61	1·90
„ —einkorn	4	8·34	14·67	2·19	55·67	13·56	5·57
„ —emmer	25	8·68	13·24	1·89	60·85	11·27	4·07

but widely disseminated in Canada and the United States, which retains in England something of the high nitrogen content and strength characteristic of North-Western America, and nearly always shows a nitrogen content of well over 2 p.c. (*see* Hall, J. Board Agric. 1904, 11, 321; Humphries and Biffen, J. Agric. Sci. 1907, 2, 1; papers read at the Winnipeg meeting of the British Association, Jour. Board Agric. 17, 1910). Moreover, Biffen (J. Agric. Sci. 3, 1909, 86) has shown that high and low nitrogen content are Mendelian characters which segregate and are inherited without blending.

(2) Climate is more potent than any other factor in causing variations in the composition of wheat. Leclerc and Leavett (U.S. Dep. of Agric. Div. of Chem. Bull. 128, 1910) grew the same varieties of wheat in three localities with widely differing climates, and in the next year grew on seed from each locality at all three places, with the following results as regards protein content:—

Year	Origin of seed	Protein in seed	Protein in product grown in		
			Kansas	California	Texas
1906	Kansas	16·22	19·13	10·38	12·18
1907	Kansas	19·13	22·23	11·00	16·97
1907	California	10·38	22·23	11·33	18·22
1907	Texas	12·18	22·81	11·37	18·21

Thus the seed of Kansas origin and containing 19·13 p.c. of protein when grown in California in 1907 yielded grain only containing 11·00 p.c. of protein; whereas in the same year seed from the same original stock but grown in California in 1906 and only containing 10·38 p.c. protein, when moved back to Kansas, yielded grain containing 22·23 p.c. of nitrogen. In these cases, the influence of environment is enormous, and in the main the strong high nitrogenous horny wheats of the American North-West, Hungary and Russia, owe these qualities to their environment. They are spring sown when the severe winter is over; they receive considerable rainfall during their early growing months, followed by great heat with progressive dryness of the atmosphere, the cycle of growth being completed in four months or less. The soft low-nitrogenous wheats are generally winter sown with an equably distributed rainfall, as in Western Europe, though, as the experience of California, Oregon, Australia, and India show, great heat and dryness at the ripening stage will not ensure a high nitrogen content. While climates like Kansas impart a high nitrogen content to all varieties, some varieties commonly grown there, like Fife, possess a high nitrogen content congenitally and retain it in climates like the English, where other wheats with a high nitrogen content in Kansas at once deteriorate.

(3) Season has a much greater effect than manuring in altering the composition of wheat, change of season being, in this respect, comparable to change of climate and environment. The variations of English seasons, however, are never sufficient to induce 'strength' comparable to that found in the wheats of the American North-West, &c.

The table on p. 728 shows the variation in the composition of wheat grown on the experimental plots at Rothamsted in 1852, a wet cool year, and 1863, a dry and hot year.

(4) Taken by itself, soil has not a very large effect upon the character of the wheat grown; in fact, in practice it is difficult to disengage the variations due to soil from those depending on the changed environment generally, soil being, as it were, a factor in climate.

(5) The composition of wheat shows some variation with the character of the manuring, but the variations are not large. The following results were obtained with the wheat grown on the Rothamsted Experimental plots in 1893, the fortieth season in which the plots had been growing wheat with the same manures on the same land, thus setting up much more extreme differences than would occur in practice:—

Plot	Manuring	Weight per bushel lbs.	Nitrogen, p.c.	Ash, p.c.
3	Unmanured	62·7	1·997	1·84
5	Mineral, no N	62·3	2·015	2·04
6	Minerals + 43 lbs. N	63·1	2·187	1·98
7	„ + 86 lbs. N	62·5	2·401	1·92
8	„ + 129 lbs. N	62·4	2·352	1·89
10	86 lbs. N only	59·1	2·084	1·70
2	Farmyard manure	63·4	2·264	1·96

—		2 Dung	3 Unmanured	7 N P_2O_5 K_2O	10 N only	11 N P_2O_5
Weight per bushel, lb.	1852	58·20	56·60	56·00	55·90	55·60
	1863	63·10	62·70	62·60	62·60	62·50
Weight of 100 grains, grams	1852	3·46	2·88	3·08	3·26	2·94
	1863	5·35	5·02	4·79	4·51	4·76
Grain to 100 straw	1852	49·60	53·90	41·90	47·30	47·80
	1863	67·50	70·40	59·40	74·30	70·40
Nitrogen in dry grain, p.c.	1852	2·02	2·08	2·29	2·48	1·95
	1863	1·52	1·65	1·53	1·70	1·79
Nitrogen in dry straw, p.c.	1852	0·46	0·57	0·87	0·89	0·46
	1863	0·25	0·33	0·36	0·35	0·44
Ash in dry grain, p.c.	1852	1·98	2·03	1·95	1·83	1·96
	1863	1·85	1·95	1·73	1·56	1·72
Ash in dry straw, p.c.	1852	7·04	7·04	5·55	5·60	6·10
	1863	6·42	7·12	5·22	5·40	5·48

The wheats from these plots have also been ground and the flours resulting baked separately, whereupon they show extreme differences in quality and in the character of the loaf they yield (*see* Hall, *l.c.*).

(6) It will be seen from the table of composition that spring wheat possesses a higher nitrogen content than winter wheat, and it has been supposed that the difference can be correlated with the shorter period of growth of the former. Direct experiment, however, with the same variety of wheat sown at monthly intervals, did not support this view (Humphreys, *l.c.*). In the climates producing high nitrogen content and strength, the wheats must be necessarily spring sown, *i.e.* spring sowing and high nitrogen content are both results due to the same environment and are not causally related.

Similarly, the farmer's idea that early cutting gives rise to strength is not confirmed by experiment, though wheat cut green may appear somewhat horny. Again, premature ripening is associated with climates producing strength, though it is not the cause of strength.

(7) Various investigations have been made into the change of composition of the grain of wheat during its development (Pierre, Mem. Soc. Linnéene de Normandie, xv. 1869, 1, 220; Déherain, Ann. Agron. 8, 1882, 23; 20, 1894, 561; Adorjan, J. für Landw. 1902, 50, 193; Teller, Arkansas Expt. Sta. Bull. 52, 1899).

Hall and Brenchley (J. Agric. Sci. 1909, 3, 195) obtained the following results on wheat grown at Rothamsted:—

BROADBALK, PLOT 3.—1907.

Date.	Green weight of 1000 grains	Dry weight of 1000 grains	Specific Gravity	Per cent. nitrogen in dry matter.	Per cent. ash in dry matter	Per cent. P_2O_5 in ash	Per cent. dextrose in dry matter	Maltose produced by 100 of dry matter
	Grams	Grams						
July 16	13·75	3·51	1·116	2·679	3·70	33·66	—	—
„ 19	21·05	5·43	1·116	2·406	3·03	36·91	14·99	339·4
„ 22	32·47	8·14	1·113	2·458	3·14	36·88	11·08	324·7
„ 25	39·70	11·16	1·116	2·167	2·80	38·73	7·36	541·4
„ 28	45·95	14·05	1·099	2·119	2·66	38·86	6·71	650·7
„ 31	51·30	17·99	1·116	2·055	2·39	38·68	6·23	597·1
Aug. 3	56·69	21·15	1·128	1·856	2·38	40·35	3·70	510·6
„ 6	57·91	24·97	1·113	1·828	2·16	42·54	2·42	442·9
„ 9	62·48	28·98	1·196	1·801	2·16	44·17	2·17	412·0
„ 12	63·68	32·20	1·215	1·720	2·09	44·30	1·86	378·1
„ 15	63·19	35·09	1·218	1·856	1·89	44·06	1·46	277·9
„ 18	70·89	37·93	1·231	1·787	1·96	46·50	1·99	441·6
„ 21	66·30	38·69	1·204	1·846	1·94	46·13	1·91	343·7
„ 24	61·01	37·96	1·271	1·778	1·93	46·30	2·02	322·1

It will be seen that the immature grain is richer in nitrogen and ash; it also contains more ready-formed sugar, and possesses a slightly higher diastatic power. Other determinations show that in the early stages about three quarters, but at ripeness practically the whole, of the nitrogen is in the protein form. The figures, however, do not support the idea that in the later stages of filling the grain, only starch enters, the material entering the grain is of almost uniform composition throughout. In the final ripening process, desiccation is the most pronounced change setting in.

Carbohydrates of Wheat.—The carbohydrates present in wheat grain have been examined by Stone (U.S. Dep. of Agric., Office of Expt. Stations, Bull. 34, 1896), who found sucrose and reducing sugars, amylans and pentosans, in

addition to starch, which is the principal constituent of the endosperm. It has also been shown by Whymper (Int. Cong. App. Chem. London, 1909) that the larger granules of the starch contained in the endosperm are more readily attacked by the diastase secreted during germination.

The sugars are chiefly present in the germ, and among them Schulze and Frankfurter identified raffinose (Ber. 27, 1893, 64).

Proteins.—The proteins contained in wheat, and particularly in flour, have been the subject of considerable investigation; references to Ritthausen and the other earlier workers will be found in Osborne's papers (Amer. Chem. J. 1893, 15, 392; 1894, 16, 524; Amer. J. Phys. 1905, 13, 35; 1906, 17, 223; Carnegie Inst. Washington, 1907, Pub. 84), from which the following summary has been extracted:—

'The proteins of the wheat kernel are *gliadin*, insoluble in neutral aqueous solutions, but distinguished from all the others by its ready solubility in neutral 70 p.c. alcohol; *glutenin*, a protein having a similar elementary percentage composition to gliadin, soluble in very dilute acid and alkaline solutions, but insoluble in dilute alcohol or neutral aqueous solutions, and yielding a wholly different proportion of decomposition products when boiled with strong acids; *leucosin*, an albumin-like protein, freely soluble in pure water, and coagulated by heating its solution to 50°–60°; a *globulin* similar in composition and properties to many globulins found in other seeds, and one or more proteoses which are present in very small quantity. It has also been shown that the proteins obtained from the embryo of the wheat are the globulin, albumin, and proteose above mentioned, and that these form nearly all of the protein substance of this part of the seed. It thus appears that these three proteins are contained chiefly in the embryo, and that gliadin and glutenin form nearly the whole of the proteins of the endosperm, or over 80 p.c. of the total protein matter of the seed. It is possible that a part of the albumin, globulin, and perhaps minute quantities of the proteose, are contained also in the endosperm, for these proteins are always found in flour from which, in the milling process, the embryo is very nearly completely separated. . . .

'Gluten contains the greater part of the protein matter of the seed, together with a little starch, fat, lecithin, and phytocholesterin, and possibly some carbohydrate substance or substances of as yet unknown character. These non-protein substances are probably not united with one another in the gluten, but are mechanically mixed. The quantity of starch that remains in the gluten depends on the thoroughness of the washing, while the other substances owe their presence largely to their insolubility in water. The chief constituents of the gluten are the two proteids, gliadin and glutenin, the relative proportions of which vary with the variety of wheat from which the flour is made. The character of the gluten and the commercial value of the flour depend, to a large extent, on the proportion of gliadin to glutenin.

'In the moist gluten, these proteins are present combined with about twice their weight of water, which is gradually lost on exposure to dry air or at an elevated temperature.

'The gliadin and glutenin are present as such in the seed, and are not, as was formerly supposed, derived from other protein substances through the action of an enzyme. This is shown by the fact that they may be obtained directly from the flour by the same treatment as that which yields them from the gluten, and under conditions which preclude the action of an enzyme.

'The characteristics of the different wheat constituents, the products which they yield on hydrolysis, and related questions are also considered, and the nutritive value of wheat gluten and other proteins is discussed on the basis of the kind and amount of the cleavage products which they yield on hydrolysis.

'The amount of glutaminic acid which the gluten proteins yield is far greater than that yielded by any of the other food proteins, with the exception of gliadin from rye and hordein from barley. The proteins of the legumes and nuts which are used as food yield from 15 to 20 p.c. of glutaminic acid, so that the mean amount of this amino- acid from the wheat protein is nearly twice as large. The same also is true of ammonia.

'The proportion of arginine from wheat gluten is relatively small compared with that from most other seed proteins, many of which yield from 10 to 16 p.c. of this base.

'The proportion of lysine is likewise small, especially compared with that obtained from the leguminous seeds. The amount of histidine, however, does not differ very greatly from that of the other seed proteins. What significance these differences have in respect to the nutritive value of these different proteins must be determined by future investigation, for it has only very recently been discovered that such differences exist.'

Fat.—Wheat contains about 1·5 p.c. of fat, the highest proportions being found in the wheats from the Canadian North-West. It is mostly present in the germ, in which it may amount to 15 p.c. This oil easily turns rancid, and is characterised by a high iodine number (115).

Ash.—Analyses of the ash of wheat may be found in Wolff, Aschenanalysen, Berlin, 1871 and 1880; Lawes and Gilbert, Chem. Soc. Trans. 1884, 45, 305.

The table on p. 730, from unpublished Rothamsted records, shows the variations induced by manuring in 1896, the forty-fourth season in which the wheat had been grown on the same plots with the same manures.

Mill products of Wheat.—An account of the various products obtained during the conversion of wheat into flour, with analyses, is contained in Part 9, Bull. 13 (1898) U.S. Dep. of Agric. Div. of Chem. *See also* Maurizio, Getreide Mehl u. Brot. Berlin, 1903.

Baking qualities of Wheat Flour.—The earliest attempt to determine the quality of flour in a baker's sense, *i.e.* the power of the flour to produce a large firm loaf, consisted in estimating the weight of gluten that could be kneaded out of a given weight of flour. While this test proved to be of value in comparing flours from similar wheats or from wheats grown in the same locality, so many exceptions occurred that no absolute value could be attached to the test.

BROADBALK WHEAT GRAIN—SEASON 1896.

Plot	2b	3 and 4	6	8	10ab	11	12	13	14
Ash in dry matter .	1·90	1·84	1·88	1·74	1·57	1·72	1·78	1·76	[c]1·76
Nitrogen in „ .	2·115	1·835	1·849	2·101	1·94	1·931	1·949	1·875	1·954 [c]
Ferric oxide . .	0·67	0·84	0·81	0·76	0·98	0·735	0·755	0·744	0·695
Lime . . .	2·40	3·30	2·70	3·00	4·91	4·63 [c]	4·00	3·21	4·23
Magnesia . .	10·87	10·28	10·31	10·50	10·10	9·86	9·96	9·93	10·36
Potash . . .	31·75	33·62	33·08	33·23	34·79	32·33	32·62	33·97	32·21
Soda . . .	0·036	0·101	0·007	0·084	0·196	0·105	0·115	0·078	0·114
Phosphoric acid .	51·70	48·34	49·61	48·97	43·07	48·09	48·30	48·79	47·83
Sulphuric acid . .	0·89	1·52	1·26	1·28	3·38	1·49	1·39	1·22	1·49
Chlorine . . .	0·020	0·395	0·054	0·205	0·973	0·199	0·138	0·088 [c]	0·279
Silica . . .	0·46	0·55	0·53	0·43	0·64	0·46	0·48	0·45	0·45
Sand and charcoal .	1·29	1·38	1·86	1·61	1·40	2·30	2·18	1·45	2·39

Estimates based on the total nitrogen in the flour proved to be subject to the same errors. Measurements were then made of the gliadin, the wheat protein soluble in 70 p.c. alcohol; Fleurent further suggested that the ratio of the gliadin to the glutenin in the gluten determined its quality; but these methods in turn broke down under criticism (*see* Hall, *l.c.*). T. B. Wood (Jour. Agric. Sci. 1908, 2, 139, 267) regards baking quality as dependent on two factors: the size of the loaf is determined by the amount of sugar contained in the flour, together with that produced in the dough by diastatic action. This determines the evolution of carbon dioxide, both as to rate and total amount. Then the quality of the gluten, which determines how the dough will stretch under the evolution of the carbon dioxide, depends on its physical character, which will vary enormously according to the state of equilibrium between the colloid gluten and the salts in the water with which it is in contact. Under certain conditions the gluten loses all consistency, its physical character being entirely conditioned by the surrounding liquid. (For other views on this intricate subject, *see* the British Association papers on wheat (*l.c.*).)

Nutritive Value of Wheat.—The nutritive value of various samples of wheat has been calculated by Chamberlain (U.S. Dep. of Agric. Div. of Chem. Bull. 120, 1909) as follows:—

Variety	Water	Digestible constituents				Ash	Production value calories per 100 lbs.	Albuminoid ratio
		Protein	Fat	Carbohydrates	Crude fibre			
North-West spring	10·11	11·78	1·41	73·04	1·17	1·85	94,717	6·6
Soft winter . .	10·55	9·96	1·20	75·24	1·17	2·00	94,760	7·9
Durum . .	9·77	13·02	1·72	70·77	1·33	2·02	94,457	5·8

The analyses give the digestible as distinct from the total constituents of the wheat, and in the last column but one the value of the wheat for the production of energy or increased weight is expressed as calories developable from 100 lbs. of the grain, after allowance has been made for the non-digestible portions and the work consumed in the process of digestion. The last column gives the ratio of the non-nitrogenous constituents [digestible carbohydrates and fibre + digestible fat × 2·25] to the digestible proteins.

Wheat Straw.—The composition of wheat straw is more variable than that of the grain: the more complete the ripening process the more thoroughly will the carbohydrates, proteins, and valuable ash constituents of the straw be transferred to the grain. The variations in the composition of the straw in response to different conditions of soil and manuring, are minimised in the grain, which the plant endeavours to make of as constant a composition as possible. The following table (König) gives a few typical analyses of straw, which are followed by a table of the mean composition of the ash of straw from wheat grown on the Rothamsted plots, to illustrate the variation with manuring:—

Origin	No. of samples	Water	Fat	Protein	N. free extract.	Crude fibre	Ash
English winter sown .	—	13·6	1·3	3·3	39·4 [1]	37·1	5·3
German „ .	—	14·3	1·2	3·0	35·9	40·8	4·85
American spring „ .	7	9·6	1·3	3·4	43·5	38·0	4·2

[1] Carbohydrates.

BROADBALK WHEAT STRAW—MIXED SAMPLES, 10 YEARS, 1882–91.

Plot	2	3	5	7	10	11	12	13	14
Ash in dry matter	8·13	7·69	7·95	5·89	6·02	5·84	5·69	5·93	5·52
Ferric oxide	0·31	0·94	0·60	0·50	0·54	0·43	0·33	0·34	0·41
Lime	3·64	4·38	3·49	5·68	8·36	9·14	7·71	5·38	7·70
Magnesia	1·51	1·51	1·41	1·76	2·29	2·25	1·92	1·53	2·46
Potash	18·41	13·51	16·30	25·84	13·67	9·92	14·65	23·23	14·88
Soda	0·09	0·10	0·09	0·21	0·41	0·58	0·57	0·03	0·33
Phosphoric acid	3·87	2·97	4·24	3·81	2·26	4·26	3·64	3·38	3·87
Sulphuric acid	3·44	3·81	4·76	5·40	6·72	5·44	5·32	5·06	5·31
Chlorine	2·92	1·81	1·90	6·59	2·72	1·66	2·88	5·60	2·81
Carbonic acid	[1]	[1]	[1]	[1]	1·25	trace	none	none	trace
Silica	64·64	67·70	65·14	49·59	60·44	65·20	61·79	54·16	61·08
Sand and charcoal	1·41	3·78	2·27	1·93	2·23	1·52	1·62	2·36	1·81

Methods of Analysis.—In the analysis of wheat, the ordinary methods employed for feeding stuffs are followed, the only special determinations required being those of gluten and gliadin.

For the determination of gluten, 20 grams of dry flour, or of the ground wheat from which the husk has been sifted, are weighed out on to a piece of bolting silk, about 8 inches square, moistened with water and kneaded up into a paste. The silk is then gathered together over the dough and kneaded in several changes of water or under a tap until no more starchy liquid flows away, being finally kneaded in the air until it ceases to lose water. The gluten will then generally form an elastic coherent mass which can be removed from the silk without loss, weighed in its wet condition, spread on a tared sheet of glass or porcelain basin, dried at 100° to a constant weight, and weighed again. The ratio between wet and dry gluten is regarded as of some importance.

For gliadin, 5 grams of flour are put in a flask with 250 c.c. of 70 p.c. alcohol, and shaken in a machine for 6 hours. The mixture is then rapidly filtered, and 100 c.c. of the solution are placed in a Kjeldahl flask. The alcohol is distilled off and the nitrogen in the residue is determined in the usual way. Nitrogen × 5·68 = gliadin.

Barley. Barley generally shows a smaller protein content than wheat; this difference is not only characteristic of the two species, but barleys are likely to have been unconsciously selected for low protein content, this being the quality most desired by the brewer, who has always been the chief purchaser of barley. The adherent glume and pale further cause an increase in the crude fibre and ash, as compared with wheat.

The following analyses of barley are derived, 1–6 from the author, 7 from König (*l.c.*), and 8 and 9 from Wiley (*l.c.*);—

	Number of analyses	Water	Fat	Proteins	Carbo-hydrates	Crude fibre	Ash
English Chevalier—							
1899—grown after roots	21	16·23	1·65	9·69	66·06[1]	4·10	2·27
1899— „ „ wheat	7	16·44	1·31	9·12	66·05[2]	4·64	2·44
1900—prize winners	7	16·30	1·50	7·81	68·36[3]	3·80	2·23
1900—poor quality	4	16·80	2·28	10·78	64·24[4]	3·82	2·08
Chili Chevalier, 1900—prize	1	15·6	2·06	9·44	67·04[5]	3·61	2·25
Asia Minor, four-rowed—prize	2	15·3	1·86	8·75	67·47[6]	4·38	2·24
Germany, Middle and North	120	14·05	1·80	9·88	66·75	4·77	2·75
United States	32	10·8	2·13	10·69	69·89	4·05	2·44
Canada	20	11·96	2·06	10·57	68·90	4·10	2·41

The composition of barley is affected by climate, environment, manuring, &c., in the same way as the composition of wheat, barley being somewhat more susceptible to change. The commercial value of barley varies also to a much greater degree; not only are there two distinct grades—barley for malting and barley for feeding purposes, the price of the former being nearly 50 p.c. higher than that of the latter, though the two kinds grade off into one another—but special prices are paid for barley of exceptional quality.

(1) Variety. The number of barley varieties is small compared with that of wheat. The two-rowed varieties fall into two types, wide and narrow eared, and are most prized for brewing

[1] Not determined.

[1] Containing starch, 57·9 p.c.
[2] Starch = 54·2 p.c.
[3] Starch = 61·5 p.c.
[4] Starch = 58·0 p.c.
[5] Starch = 61·2 p.c.
[6] Starch = 62·4 p.c.

purposes. The four-rowed and six-rowed types are not so much used for brewing. Strictly comparative analytical data are lacking.

(2) The following data, drawn from the Rothamsted records, show the effect of season and manuring upon the character of the barley—in 1893, a summer of extreme heat and dryness, and 1894, a wet and cool season:—

Plot	Manuring	Yield of grain		Weight per bushel		Grain to 100 straw		Nitrogen per cent. in grain	
		1893	1894	1893	1894	1893	1894	1893	1894
		Bush.	Bush.	lb.	lb.				
10	Unmanured	8·3	10·0	55·6	51·1	71·9	70·3	1·899	1·409
40	Minerals, no N	9·9	13·1	56·1	52·1	74·3	79·2	2·011	1·467
1A	N only	11·6	10·4	55·1	50·4	85·3	67·5	2·188	1·646
2A	N, P_2O_5, no K_2O	18·1	34·9	54·0	51·9	101·0	77·0	2·129	1·600
3A	N, K_2O, no P_2O_5	16·8	17·8	55·8	51·5	85·9	73·8	2·171	1·614
4A	N, K_2O, P_2O_5	30·8	41·4	56·3	54·1	102·2	77·7	2·081	1·440

The following results, also obtained at Rothamsted, show the effect of nitrogenous manuring:—

—	Dressed grain. Weight per bushel lbs.	Grain to 100 straw	Offal grain to 100 dressed grain	N in dressed grain p.c.
No nitrogen . .	58·0	110·4	5·9	1·61
86lbs. per acre organic N	57·3	96·6	12·5	1·79
86 lbs. per acre organic N in the previous year	55·1	72·8	34·9	2·42

These results confirm the general opinion that barley for malting purposes should not be grown on land that is in high condition, either as a result of its previous treatment or through the recent application of nitrogenous fertilisers.

Composition of Barley.—(*a*) Carbohydrates. Barley contains soluble sugars, which may amount to 4 p.c. of the dry grain; sucrose is the chief constituent, but dextrose is also found, and O'Sullivan has shown the presence of raffinose. The main carbohydrate present is starch, of which H. T. Brown and his colleagues found 55·5 p.c. in the dry material of 10 barleys examined (Trans. Guinness Research Lab. 1903, 1, 91). The same investigators (*l.c.* 1906, 2, 312) proceeded to the determination of certain water soluble polysaccharides, called by O'Sullivan amylans, which yield on acid hydrolysis a racemic acid, glucose, arabinose and xylose. They further showed that the sum of the sugars, starch, and amylans, with a little ash and soluble protein, made up the whole of the barley grain that goes into solution when the barley is extracted with boiling water and hydrolysed with malt extract. They obtained from 9·5 to 10 p.c. of amylans on the dry weight of various samples of barley examined.

In the 'grains' not rendered soluble by diastase, there are considerable quantities of 'furfuroids' to be found, besides cellulose and fibre.

(*b*) Osborne and Ritthausen have examined the proteins of barley, and Osborne (J. Amer. Chem. Soc. 1895, 17, 539) obtained 4·5 p.c. of an insoluble protein, 4 p.c. of hordein soluble in dilute alcohol, 0·3 p.c. of leucosin, and 1·95 p.c. of edestin and proteose soluble in water. It has also been shown that a small proportion of the nitrogen of barley is not combined as protein.

(*c*) The ether extract of barley is found to contain neutral fats, free fatty acids, and lecithin.

(*d*) The following analyses show the composition of the ash of barley from the Rothamsted plots in 1871:—

BARLEY—SEASON 1871.

—	1 0 Unmanured		4 0 Complete minerals		1 A Nitrogen only (as ammonia)		4 A Nitrogen and minerals		1 C Nitrogen only (as rapecake)		7 Farmyard dung	
	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw
Ash in dry matter	2·64	6·17	2·77	6·96	2·38	5·51	2·64	6·70	2·84	5·54	2·87	7·55
Ferric oxide .	0·49	0·78	0·41	0·46	0·35	0·35	0·31	0·44	0·35	0·42	0·31	0·31
Lime . . .	2·91	10·04	2·67	7·21	3·29	9·91	2·51	7·56	2·31	9·52	2·22	6·56
Magnesia . .	7·70	1·96	7·65	1·44	7·95	1·97	8·07	1·89	7·91	2·18	7·75	1·30
Potash . .	29·16	19·07	29·87	27·36	28·80	17·11	30·67	33·90	28·89	26·84	29·23	29·39
Soda . . .	1·30	5·85	0·50	1·93	2·16	13·24	0·68	2·16	0·56	2·93	0·40	2·53
Phosphoric acid .	34·05	3·18	35·95	4·30	30·74	1·87	35·64	3·17	36·39	5·44	36·72	3·76
Sulphuric acid .	2·24	5·53	2·15	7·26	2·19	4·51	1·56	5·54	1·60	6·02	1·65	3·27
Chlorine . .	1·71	6·96	0·71	7·72	3·57	15·10	0·86	14·58	0·68	4·55	0·31	11·99
Silica . .	19·62	44·49	18·99	42·63	18·57	37·98	20·38	32·71	19·85	42·04	21·02	42·71
Sand and charcoal	1·67	3·52	1·40	2·18	2·84	1·64	0·93	2·13	1·80	1·87	0·86	1·68

Barley Products.—The chief material prepared from barley is 'pearl barley,' in which the husk and germ have been removed mechanically. This material is also sometimes ground into barley flour. Important by-products for cattle feeding are also the 'grains' obtained in the brewing process after the diastatic extraction of the starch contained in malt, and the malt culms or sprouts knocked off the partly germinated barley after malting. Analyses are given below:—

	Water	Fat	Proteins	Carbo-hydrates	Crude fibre	Ash
Pearl barley	14·9	1·0	7·6	75·1	0·6	0·8
Malt culms	11·8	2·1	28·3	42·8	12·4	7·6
Brewer's grains (wet)	75·0	2·0	5·5	12·0	4·5	1·0
" " (dry)	10·0	7·0	20·0	42·0	16·0	5·0

Maize. Maize or Indian corn is a cereal grain characterised by a high proportion of carbohydrates and oil but comparatively low protein and ash. Its composition does not vary to the same degree as that of wheat or barley. The following average analyses are derived from Wiley (U. S. Dep. of Agric. Div. of Chem. Bull. 50, 1898) and König (*l.c.*):—

Source.	No. of samples	Moisture	Crude fat	Proteins	Carbo-hydrate	Crude fibre	Ash
United States, Mean	—	10·75	4·25	10·00	71·75	1·75	1·50
" " Northern	—	9·98	5·11	10·64	71·32	1·41	1·54
" " Middle West	—	12·33	4·97	10·89	68·16	2·22	1·43
" " Pacific slope	—	9·78	6·40	8·14	72·13	2·07	1·48
Italy	—	13·13	3·84	10·26	67·72	2·88	1·95
Germany (1880)	14	13·00	5·11	8·62	70·54	1·38	1·34
Hungary (1880)	38	13·00	3·85	9·06	71·10	1·69	1·30

The only variation in composition worthy of note is that in 'sweet corn,' varieties of which are grown in America to yield immature cobs for boiling as a vegetable, the grains contain a higher proportion of sugar than is normal, especially in the immature state, and also a greater amount of oil.

Maize oil is expressed in considerable quantities from the germ, which is removed in preparing meal from the grain. It is a light amber-coloured tasteless oil used for salad oil, as a lubricant, and for soap making.

Carbohydrates.—Less than 1 p.c. of sugar is present in maize, the greater part bring sucrose with a small amount of reducing sugar. Starch is the principal carbohydrate, but a little dextrin or other gum-like body has been found, also furfuroids and pentosans up to about 5 p.c.

Proteins.—Osborne has isolated from maize, *myosin*, *vitellin* and another unnamed *globulin*, small quantities of two albumins, and *zein*, the characteristic protein which exists in both a soluble and insoluble form. It is noteworthy that zein, on hydrolysis, yields no lysin and no tryptophan, and certain defects in the nutrition of animals fed on maize alone have been set down to the lack of these groups in the zein molecule.

Ash.—The following table from Wolff's Aschenanalysen gives the average composition of the ash of maize:—

	P.c. ash in dry	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2
Red German	1·30	24·33	1·50	3·16	16·00	1·88	49·36	1·00	2·77
American	1·28	26·75	3·85	2·56	15·24	2·00	47·47	1·20	1·93
German	1·72	25·73	—	2·03	17·35	1·51	43·80	—	4·99

Maize Products.—Maize is ground into a meal, 'corn flour,' the germ and the more flinty portions of the grain being removed, and the composition of the meal is set out in the table below, in which is also given the composition of maize 'stover,' *i.e.* the stalk, leaves, &c., without the cob.

A large number of commercial products are derived from maize, especially starch and glucose; and the manufacturing processes give rise to various by-products—maize germ meal, gluten feed, &c., used for feeding cattle, but their composition depends entirely upon the method by which they are prepared.

	Moisture	Oil	Proteins	Carbo-hydrates	Crude fibre	Ash
Corn flour: three samples	12·57	1·33	7·13	78·36	0·87	0·61
Maize stover	19·81	2·56	4·19	42·87	26·02	4·55

Oats. From the food point of view, oats form one of the most valuable of the cereals, being exceptionally rich in oil and protein; it is only the adherent husk which prevents them from being the most concentrated of all the food grains. Oats show considerable variations of composition, as the following analyses indicate:—

Origin	No. of Analyses	Water	Fat	Protein	Carbo-hydrates	Crude fibre	Ash	——
Middle and North German	103	12·11	5·30	10·82	58·23	10·25	3·29	König
French	196	12·11	5·46	9·52	60·47	9·18	3·26	„
American	22	12·11	4·96	11·26	59·35	9·33	2·99	„
„ (World's Fair)	72	9·96	4·42	12·07	58·28	11·92	3·35	Wiley[c]
Scotch	10	16·90	5·59	11·57	57·54	8·25	2·59	Aitken[1]
Oatmeal	16	7·30	7·20	16·10	67·50	0·90	1·90	Atwater[2]
Oatstraw (Scotch)	10	15·32	3·45	3·04	52·59	33·95	6·96	Aitken[1]

As might be expected, the composition of oats varies with variety, climate, season, and manuring, in much the same way as wheat does. Of these variations, those due to the variety of oat are of most importance, particularly in the manufacture of oatmeal. The proportion of husk to kernel is of most significance, and the individual Scotch analyses, of which the mean is given in the table above, show variations in the fibre of from 6 to 14 p.c., and in oil, the other variable constituent, of from 4 to over 8 p.c. Wilson (Trans. H. of Ag. Soc. 1903, v. 15, 183) gives figures relating to the amount and composition of the oatmeal obtained from several varieties of oats grown on the same experimental area in Aberdeen, as follows:—

Variety	Year	Husk, p.c.	Oatmeal, p.c.	Oil in oatmeal, p.c.	Protein in oatmeal, p.c.
Dun	1901	21·98	66·21	7·68	14·37
„	1902	21·36	64·13	7·74	15·50
Potato	1901	22·24	66·32	9·59	15·44
„	1902	22·47	64·02	10·01	12·31
Newmarket	1901	21·79	66·65	4·60	14·37
„	1902	20·46	64·84	6·63	13·50

Other Cereal Grains and Products therefrom. Of the very large number of other cereal grains consumed as food, the following are among the most important:—

——	No. of samples	Water	Crude fat	Crude protein	Carbo-hydrates	Crude fibre	Ash	Authority
Rye								
German	63	13·37	1·84	11·52	68·88	2·55	1·94	König
American (World's Fair)	18	10·62	1·65	12·43	71·37	2·09	1·92	Wiley
Rice								
unhulled	—	10·50	1·60	7·50	67·40	9·00	4·00	Wiley[3]
hulled	—	12·00	2·00	8·00	76·00	1·00	1·00	
polished	—	12·40	0·40	7·50	78·80	0·40	0·50	
Millet (*Panicum miliaceum*)								
unhulled	6	12·50	3·89	10·61	61·11	8·07	3·82	König
„	34	9·00	3·25	12·83	71·50	8·84	3·58	Chamberlain
hulled	9	11·79	4·26	10·51	68·16	2·48	2·80	König
Sorghum saccharatum	38	15·17	3·36	9·26	67·99	2·51	1·71	„
„ *vulgare*	12	11·46	3·79	8·96	70·25	3·59	1·95	„
Andropogon sorghum	10	—	3·25	11·71	81·58	1·80	—	Chamberlain

Chamberlain (*l.c.*) has calculated the feeding value of the cereal grains of American origin as follows—

	Production value, cals. per gram	Starch equivalent	Albuminoid ratio
Wheat	2·08	88·1	6·5
Barley	1·99	84·2	8·0
Oats	1·70	72·0	5·8
Maize	2·23	94·2	12·3
Emmer	1·64	69·4	6·0
Einkorn	1·60	67·8	5·2
Rye	2·08	88·2	6·9
Panicum miliaceum	1·84	78·1	11·5
Andropogon sorghum	2·06	87·2	10·5

The production value represents the number of calories of energy available from the gram of food, after deduction has been made for the energy in the excreta and the energy consumed in digestion processes. The starch equivalent gives the effect of 100 lbs. of these foods in the production of fat or external work in terms of lbs. of pure starch required to produce the same effect.

A. D. H.

CEREBRIN *v.* ENZYMES.

CEREBROSE (Galactose) *v.* CARBOHYDRATES.

CERESIN. Ceresin occurs in commerce in the form of thin round masses several inches in diameter, harder than wax, of a dazzling white appearance; inodorous, and transparent at the edges.

[1] Trans. H. & Ag. Soc. 1901, v. 13, 292 and 293.
[2] U.S. Dep. of Agric. Office of Expt. Sta. Bull. 28, 1899.
[3] Type analyses from various data.

The fracture is somewhat similar to that of wax, but ceresin does not become plastic in warm water. The melting-point is between 75° and 80°. It is not attacked by acids, either in the cold or when heated; nor by alkalis, which do not saponify a trace of it. It is entirely volatilised at a high temperature without alteration. Ceresin is apparently a paraffin; it does not appear to be obtained from coal tar, but from Galician 'earth-wax,' *i.e.* ozokerite. It is used as a substitute for beeswax (J. Soc. Chem. Ind. 11, 372).

CERIN and **CERYL CEROTATE** *v.* CORK; WAXES.

CERISE. A trade name for a variety of aniline red and acid magenta.

CERIUM. Symbol Ce. At. wt. 140·25 (H. Robinson, Proc. Roy. Soc. 1884, 37, 150; Branner and Batěk, Zeitsch. anorg. Chem. 1903, 34, 103, 207). The metal has been prepared by (1) the electrolysis of the fused chloride with or without an admixture of barium or calcium chloride or alkali chloride; (2) the electrolysis of a mixture of cerium dioxide and cerium fluoride (Borders and Stockem, D. R. P. 172529; Muthmann and Weiss, Annalen, 1902, 320, 231; 1904, 331, 1; 1907, 355, 116). By the latter process, the yield corresponds with 57 p.c. of a current of 750 amperes and 7·5 volts with current densities of 9–10 amperes and 3 amperes per sq. cm. at cathode and anode respectively.

Metallic cerium has the colour and lustre of iron; its hardness is comparable with that of silver or tin; m.p. 623°; sp.gr. of fused product of electrolysis 6·728; sp.heat 0·04479 (at. heat 6·28); heat of combustion of 1 gram, 1603·15 cals. Cerium is paramagnetic; magnetic susceptibility, $(K)+182·2.10^{-6}$ (Monatsh. 1899, 20, 369). In dry air the metal is moderately stable, but becomes superficially tarnished with yellow dioxide; it decomposes water slowly in the cold, more rapidly on warming. The temperature of ignition in oxygen is about 150°–180° (Annalen, 1903, 325, 261). The metal is malleable and ductile; the wire burns even more brightly than magnesium, and combines readily with the halogens. Cerium is readily dissolved by dilute acids, but concentrated nitric acid produces a brown deposit consisting mainly of dioxide. Alloys have been prepared by melting cerium with other metals under molten sodium and potassium chlorides; the combination with aluminium, magnesium, or zinc is attended by a generation of heat (Annalen, 1904, 331, 46); liquid and solid cerium amalgams have also been obtained.

When scratched or rubbed with a steel edge, cerium emits brilliant sparks, and this property has been utilised in the preparation of gas lighters.

Separation and purification of ceria.—Of all the rare earth oxides, ceria is most readily isolated in a pure state, and the following methods have been employed in separating this oxide from lanthana, praseodymia and neodymia:—

(1) Treatment of the hydroxides suspended in aqueous caustic alkalis with chlorine; ceric hydroxide remains undissolved, while the other hydroxides are converted into soluble chlorides and hypochlorites (Mosander, J. pr. Chem. 1842, 30, 276; Mengel, Zeitsch. anorg. Chem. 1899, 19, 67).

(2) The mixed oxides dissolved in hot nitric acid and the solution evaporated down with ammonium nitrate until ceric ammonium nitrate separates. The double salt is crystallised from nitric acid until the oxide left on ignition has a light-yellow colour (Auer von Welsbach, Monatsh. 1884, 5, 508; Schottländer, Ber. 1892, 25, 378).

(3) The solution of mixed nitrates neutralised with ammonia and boiled with magnesium acetate and hydrogen peroxide whereby cerium is completely precipitated as a basic acetate (Meyer and Koss, Ber. 1902, 35, 672).

(4) The mixed ammonium double nitrates boiled with aqueous ammonium persulphate, calcium carbonate being gradually added to keep the solution neutral. The precipitate contains all the cerium as ceric nitrate and sulphate mixed with calcium sulphate (Witt and Theel, Ber. 1900, 33, 1315; *cf.* Meyer and Marckwald, *ibid.* 3003).

(5) The joint action of potassium permanganate and a basic substance (mercuric oxide, zinc oxide, magnesia, sodium carbonate, &c.) in neutral solution. The precipitate contains all the cerium as ceric hydroxide (Stolba, Ber. böhm. Ges. Wiss. 1878; Drossbach, Ber. 1896, 29, 2452; D. R. P. 143106; Meyer, Zeitsch. anorg. Chem. 1903, 37, 378).

The last of the foregoing methods is generally applicable to the mixed oxides of the rare earths, and permits of the complete separation of cerium in one operation. These processes require to be repeated before the cerium is completely freed from the last traces of lanthanum; thorium also is removed completely, only with some difficulty. The solution of nitrate, mixed with an excess of ammonium carbonate, is treated with ammonia when the greater portion of the thorium is precipitated. To remove the remainder, anhydrous cerium sulphate is prepared and added to ice-cold water, when the pure hydrated salt separates (Wyrouboff and Verneuil, Compt. rend. 1897, 124, 1300; Urbain, Ann. Chim. Phys. 1900, [7] 19, 184; Brauner, Zeitsch. anorg. Chem. 1903, 34, 103; Meyer, *ibid.* 37, 378; Orloff, Chem. Zeit. 1906, 30, 733; 1907, 31, 562; Neish, J. Amer. Chem. Soc. 1909, 31, 517).

Cerium forms several series of compounds derived from the oxides Ce_2O_3, Ce_4O_7(?), CeO_2, and CeO_3.

CEROUS COMPOUNDS.

Cerium hydride CeH_3(?). Cerium combines readily with hydrogen at 250°–270°, yielding a brownish-black amorphous hydride which not improbably consists to some extent of CeH_4. This product is stable in dry air at the ordinary temperature, but on heating it is converted explosively into cerium oxide and nitride (Matignon, Compt. rend. 1900, 131, 891; Muthmann and Kraft, Annalen, 1903, 325, 281).

Cerous fluoride $2CeF_3,H_2O$ (Jolin, Bull. Soc. chim. 1874, [2] 21, 533), known also in the anhydrous condition, and employed in the electrolytic production of the metal (*v. supra*; and *cf.* Brauner, Ber. 1881, 1944; 1882, 109, 115; Monatsh. 1882, 3, 1).

Cerous chloride $CeCl_3,7H_2O$ or $2CeCl_3,15H_2O$ (J. Amer. Chem. Soc. 1894, 16, 649; Ber. 1902, 35, 2622).

The anhydrous chloride, a fusible deliquescent

crystalline mass, is obtained by the following methods:—

(1) Heating the dry oxalate or cerium dioxide in hydrogen chloride (Robinson, Proc. Roy. Soc. 1884, 37, 150).

(2) Decomposing cerium carbide with chlorine or hydrogen chloride.

(3) Reducing anhydrous cerous sulphate to sulphide by heating in hydrogen sulphide and decomposing the latter with hydrogen chloride (Ber. 1899, 32, 3413). Cerous sulphide and hydrogen bromide yield cerous bromide.

(4) The anhydrous sulphate, when heated in a current of chlorine and sulphur chloride vapour, is converted directly into cerous chloride.

The dry chloride is readily soluble in alcohol and ebullioscopic determinations of the molecular weight in this solvent gave numbers corresponding with $CeCl_3$ (Muthman, Ber. 1898, 31, 1829).

Cerous hydroxide $Ce(OH)_3$, a white precipitate obtained from soluble cerous salts with ammonia or caustic soda, is stable only in absence of oxygen. Exposed to air it becomes slowly oxidised to yellow ceric hydroxide, passing through an intermediate reddish-violet stage $xCe(OH)_3.yCe(OH)_4$ (J. Amer. Chem. Soc. 1894, 18, 649).

Cerous oxide has not been isolated with certainty, since the ignition of decomposable cerous salts (nitrate, sulphate, oxalate, &c.) leads to the production of cerium dioxide. The reduction of the latter oxide with hydrogen at high temperatures gives rise to an unstable dark-blue oxide approximating in composition to Ce_4O_7.

Cerous sulphide Ce_2S_3 (*v. supra*), a reddish or black substance (Ann. Chim. Phys. 1904, [8] 2, 193), is moderately stable in air and slowly decomposed by boiling water.

Cerium nitride CeN, obtained by heating cerium in nitrogen (Annalen, 1903, 325, 261), or by passing ammonia over heated cerium carbide (Compt. rend. 1900, 131, 865), is decomposed by water, yielding cerium dioxide, ammonia and hydrogen. An explosive cerium azide is precipitated by adding sodium azide to aqueous cerous nitrate (Curtius and Darapsky, J. pr. Chem. 1900, [2] 61, 408).

Cerous nitrate $Ce(NO_3)_3,6H_2O$, prepared by (1) dissolving cerium dioxide in nitric acid in the presence of a reducing agent; (2) decomposing cerous oxalate with strong nitric acid. When heated strongly, pure cerous nitrate leaves a residue of pale-yellow cerium dioxide, but when praseodymium nitrate is present, the residual oxide is brown (J. Amer. Chem. Soc. 1909, 31, 517).

Cerous sulphate $Ce_2(SO_4)_3$. The anhydrous sulphate is produced by dehydrating the hydrated salt at 400°. Above 500° it decomposes, leaving a residue of dioxide. A saturated solution of the sulphate at 0° deposits the dodecahydrate $Ce_2(SO_4)_3,12H_2O$ (asbestos-like needles). Above 3° this hydrate is labile, and at higher temperatures the solution of the sulphate deposits hydrates containing 9, 8, 5, and 4 molecular proportions of water. With the sulphates of ammonium, sodium, and potassium, cerous sulphate forms double sulphates isomorphous with the corresponding salts of lanthanum, neodymium, and praseodymium. In moderately strong sulphuric acid, cerous sulphate gives rise to the acid sulphate $Ce(HSO_4)_3$ (Brauner and Picek, Zeitsch. anorg. Chem. 1904, 38, 322). This acid salt has been recommended as an oxidising catalyst in the production of aniline black, 0·3 gram of cerous oxide in this form sufficing to develop the black from 6 kilos. of aniline hydrochloride.

Cerous carbonate $Ce_2(CO_3)_3,5H_2O$, prismatic crystals, precipitated from solutions of cerous salts by ammonium carbonate, forms soluble crystallisable double carbonates with the alkali and ammonium carbonates.

Cerous oxalate $Ce_2(C_2O_4)_3,10H_2O$, crystalline white precipitate (Power and Shedden, J. Soc. Chem. Ind. 1900, 19, 636), has been used medicinally as a sedative in sickness, particularly that of pregnancy, also in chronic diarrhœa, hysteria, epilepsy, and migraine.

For other cerous salts of organic acids, *v.* Biltz, Annalen, 1904, 331, 334; Wolff, Zeitsch. anorg. Chem. 1905, 45, 89; Morgan and Cahen, Chem. Soc. Trans. 1907, 91, 477; Pharm. J. 1907, 78, 428; Rimbach and Kilian, Annalen, 1909, 368, 110.

Cerous phenoxide has been recommended as a non-irritant disinfectant (J. Soc. Chem. Ind. 1909, 1221; D. R. P. 214782).

Cerous acetylacetonate $Ce(CH_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CH_3)_3,3H_2O$, obtained by the interaction of cerous ammonium nitrate, acetylacetone, and ammonia (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184; Biltz, Annalen, 1904, 331, 334).

For complex cerium salts, *v.* Wyrouboff and Verneuil, Ann. Chim. Phys. 1906, [8] 9, 289; Barbieri, Atti R. Accad. 1908, [5] 17, 1, 540.

Ceric Compounds.

Cerium carbide CeC_2; microscopic crystals, sp.gr. 5·23, prepared by melting together in the electric furnace cerium dioxide (192 parts) and sugar carbon (48 parts), using a current of 300 amperes and 60 volts (Moissan, Compt. rend. 1896, 122, 357; 1897, 124, 1233). When decomposed with water, the carbide yields 75·5 p.c. acetylene, 20·5 p.c. methane, and 4 p.c. ethylene.

Cerium silicide $CeSi_2$; small crystals with a steely lustre, produced by heating cerium dioxide with crystalline silicon, stable in air and decomposed by acids (Sterba, Compt. rend. 1902, 135, 170).

Ceric oxide (*syn.* Cerium dioxide) CeO_2; light-yellow powder, sp.gr. 6·405; also in isotropic crystals, sp.gr. 6·76–7·905. The amorphous oxide is prepared by (1) the oxidation of the metal in oxygen; (2) the ignition of cerous salts (nitrate, sulphate, carbonate, oxalate) or ceric compounds (hydroxide, nitrate, sulphate). The ignited oxide is insoluble in hydrochloric or nitric acid or in dilute sulphuric acid. The crystalline form, obtained by heating the amorphous variety with sodium chloride, borax or potassium hydrogen sulphate, is quite unaffected by acids or alkalis. The dioxide is reduced with difficulty by aluminium and magnesium, when the corresponding cerium alloys are produced. For further references to cerium dioxide, *v.* Compt. rend. 1895, 120, 663; 1897, 124, 618, 1233, 1300; 125, 950; 1901, 133, 221; Ber. 1900, 33, 3003, 3506; Ann. Chim. Phys. 1904, [8] 2, 193; Zeitsch. anorg. Chem. 1903, 34, 103, 207; 37, 378).

Ceric hydroxide $Ce(OH)_4$, a yellowish precipitate obtained from soluble ceric salts by means of ammonia or the caustic alkalis. Cerous hydroxide is slowly oxidised to ceric hydroxide by atmospheric oxygen and more rapidly by mild oxidising agents.

Although ceric hydroxide is more stable than the lower hydroxide, the ceric salts are less stable than the cerous compounds. Ceric chloride itself has not been isolated, but its additive compounds, R_2CeCl_6, with the salts of organic bases (pyridine, quinoline, triethylamine, &c.) are stable in alcoholic solution.

Ceric sulphate $Ce(SO_4)_2$. The anhydrous salt is produced by heating the dioxide with strong sulphuric acid. With the diluted acid oxygen is evolved, and the resulting solution deposits, on concentration, ceri-cerous hydrogen sulphate $2Ce(SO_4)_2,Ce_2(SO_4)_3,H_2SO_4.24H_2O$ (Brauner, Zeitsch. anorg. Chem. 1904, 39, 261), and then yellow hydrated ceric sulphate, $Ce(SO_4)_2,4H_2O$. The former of these compounds corresponds with the intermediate oxide $Ce_4O_7(=2CeO_2,Ce_2O_3)$.

Ceric sulphate forms a series of double sulphates (*e.g.* $Ce(SO_4)_2,2K_2SO_4,2H_2O$) with the alkali sulphates.

Ceric nitrate $Ce(NO_3)_3{\cdot}OH,3H_2O$. This basic salt separates from a solution of ceric hydroxide in nitric acid. The normal ceric nitrate has not been isolated, but the double nitrates $R_2{}^{I}Ce(NO_3)_6$, where R^{I} is ammonium or an alkali metal, are well-defined crystalline substances, having a bright-red colour; they are very hygroscopic and readily soluble in alcohol or water. The double nitrates $R^{II}Ce(NO_3)_6,8H_2O$, where R=Mg,Zn,Ni,Co,Mn, form a well-defined series. These cerium double nitrates are quite analogous to the corresponding double nitrates of thorium.

For other ceric salts, *v.* Barbieri, Atti R. Accad. Lincei, 1907, [5] 16, 644; Ber. 1910, 43, 2214. For double ceric fluorides, *v.* Brauner, Ber. 1881, 1944; Monatsh. 1882, 3, 1; Chem. Soc. Trans. 1882, 41, 68; Rimbach and Kilian, Annalen, 1909, 368, 101.

Cerium peroxide and its derivatives. The addition of ammonia and hydrogen peroxide to a solution of a cerous salt determines the precipitation of reddish-brown *hydrated cerium peroxide* $Ce(O_2H)(OH)_3$. When cerous nitrate or chloride is added to concentrated aqueous potassium carbonate, the solution takes up atmospheric oxygen and assumes a deep-red colour. The liquid slowly deposits crystalline dark-red *potassium per-ceric carbonate* $4K_2CO_3,Ce(CO_3)_3O_3,12H_2O$. In the presence of glucose, this alkaline solution acts catalytically. When shaken in the air, oxygen is taken up and the per-ceric compound produced. On standing, this substance is reduced by the glucose to cerous salt, and the colour disappears. Repeated shaking leads to renewed production of per-ceric compound, so that oxidation and reduction proceed alternately to an indefinite extent (Pissarjewski, J. Russ. Phys. Chem. Soc. 1900, 32, 609; Zeitsch. anorg. Chem. 1902, 31, 359; Wyrouboff and Verneuil, Compt. rend. 1898, 127, 863; Job, Compt. rend. 1898, 126, 246; 1899, 128, 178, 1098; 1902, 134, 1052; 1903, 136, 45; Engler, Zeitsch. anorg. Chem. 1902, 29, 1; Ber. 1903, 36, 2642; 1904, 37, 49, 3268).

Applications of Cerium.—Metallic cerium (in the form of 'mischmetal,' *v.* CERIUM METALS), has been used in the reduction of the refractory oxides of columbium, tantalum, molybdenum, &c.

The oxidising action of cerium compounds has led to their use in photography (Lumière, Compt. rend. 1893, 116, 574), and as oxidising catalysts in organic preparations (Atti R. Accad. Lincei, 1907 [5] 16, i. 395). The oxides have been suggested for use in colouring glass (Chem. Ind. 1904, 27). Cerium salts have been employed as mordants in dyeing. In the preparation of leather, hide powder decomposes cerium salts, fixing the element in the form of hydrated oxide. The hide partially reduces ceric sulphate or ceric ammonium nitrate, absorbing oxygen and yielding a good quality of leather which has a yellow tint and resists the action of water (Garelli, Atti R. Accad. Lincei, 1907, [5] 16, i. 532).

In addition to cerous oxalate, other salts (*e.g.* hypophosphate, and double ammonium citrate, tartrate and lactate) have been utilised medicinally in the treatment of sea-sickness and nervous disorders. Incandescent gas mantles contain about 1 p.c. of ceria and 99 p.c. of thoria (Meyer and Anschütz, Ber. 1907, 40, 2639).

(For the detection and estimation of cerium, *v.* ANALYSIS.) G. T. M.

CERIUM METALS AND EARTHS. (**The Rare Earths.**) The so-called rare earths include a series of basic oxides, very similar in physical and chemical properties, which are generally found associated in certain rare minerals of complex composition (silicates, phosphates, titanates, columbates, tantalates, &c.).

The metals contained in these oxides may be divided roughly into two groups, named after the minerals *cerite* and *ytterbite*, in which the rare earths were first discovered.

The cerite metals (*cerium group*) are *cerium*, *lanthanum*, *neodymium*, *praseodymium* and *samarium*.

The ytterbite metals (*yttrium group*) include *dysprosium*, *erbium*, *europium*, *gadolinium*, *lutecium*, *scandium*, *terbium*, *thulium*, *ytterbium* (*neoytterbium*), and *yttrium*. Of the latter section, europium, gadolinium, and terbium form an intermediate series (the *terbium group*) connecting the cerium metals with the remaining rare earths of the yttrium group proper. Closely associated with these elements is the metal *thorium*, and *zirconium* is generally included in the category of the metals of the rare earths.

Historical Summary. In 1794 ytterbite, obtained from Ytterby near Stockholm, was shown by Gadolin, its discoverer, to contain a new oxide, to which Ekeberg subsequently gave the name *yttria*. From the Swedish mineral cerite, Klaproth, in 1803, isolated another new oxide which he called *ceria*. *Thoria* was isolated by Berzelius in 1828 from the silicate *thorite*, found at Brevig in Norway.

Gadolin's yttria was subsequently shown by Berzelius to contain ceria, and from cerite Mosander afterwards isolated the oxides *lanthana* and *didymia* (Annalen, 1839, 32, 235; 1842, 44, 125), and also effected a further separation from ytterbite of the earths *erbia* and *terbia* (Phil. Mag. 1843, 23, 251; J. pr. Chem. 1843, 30, 288).

In 1878 Marignac separated from crude erbia a less basic colourless component which he called *ytterbia* (Compt. rend. 1878, 87, 578), and this fractionation was speedily followed by Nilson's discovery of *scandia*, the least basic of the ytterbite earths, and its identification as the oxide of the hypothetical *ekaboron*, predicted by Mendeléeff. In the same year Cleve effected a further separation of the old 'erbia' into three components, of which one, namely *thulia*, is still regarded as the oxide of an element *thulium* (Compt. rend. 1879, 89, 478, 708). The doubt expressed by Marignac as to the homogeneity of didymia was shared by Delafontaine, on the ground of spectroscopic evidence (Compt. rend. 1878, 87, 634), and substantiated by Lecoq de Boisbaudran (Compt. rend. 1879, 88, 323), who isolated from this earth the less basic oxide *samaria*. The didymia left after the removal of the last-mentioned oxide was still regarded as a mixture by Brauner (Monatsh. 1882, 3, 486; Chem. Soc. Trans. 1882, 43, 278), and in 1885 Auer von Welsbach, by fractional crystallisation of the double didymium nitrates of ammonium and potassium, succeeded in separating this earth into two components, which he named *neodymia* and *praseodymia* (Monatsh. 1885, 6, 477). Lecoq de Boisbaudran now showed that Cleve's *holmia* was a mixture containing a new constituent *dysprosia* (Compt. rend. 1886, 102, 1003), the simple nature of which was afterwards confirmed by Urbain (Compt. rend. 1904, 139, 736, and 1905, 141, 521).

Gadolinia, which had been recognised by Marignac in *samarskite* (Compt. rend. 1880, 90, 899), was isolated in a more definite form by Lecoq de Boisbaudran (Compt. rend. 1889, 108, 165; 1890, 111, 409, 472), and by Bettendorf (Annalen, 1890, 256, 159; 1891, 263, 164; 1892, 270, 376), and further purified by Demarçay and by Urbain and Lacombe (*v.* GADOLINIUM). Further researches by Demarçay on Cleve's samaria led to the isolation of *europia* (Compt. rend. 1896, 122, 728), an earth provisionally symbolised as Σ, and afterwards shown to be identical with oxides indicated by the symbols Z_ϵ and Z_ξ (Lecoq de Boisbaudran, Compt. rend. 1892, 114, 575; 1893, 116, 611, 674) and S_β (Crookes, Compt. rend. 1885, 100, 1380, 1495; Proc. Roy. Soc. 1885, 38, 414).

Terbia, which occurs only in small amount in ytterbite, has been isolated in a purified state by Urbain (*v.* TERBIUM), and Marignac's ytterbia (*l.c.*) has been fractionated by Auer von Welsbach (Monatsh. 1906, 27, 935), and separated into two components, *neoytterbia* and *lutecia*, by Urbain (Compt. rend. 1907, 145, 759).

Occurrence (*v.* Das Vorkommen des seltenen Erden, Schilling, 1904; Phipson, Chem. News, 1896, 73, 145). The following is a short description of the most important sources of the rare earths:—

1. *Minerals containing chiefly Cerium Earths.*

Cerite (ochroite, cererite, cerinstein), a hydrated silicate containing 60–70 p.c. of cerium and its allies, together with smaller amounts of iron, calcium, and the yttrium earths, found in the Bastnäs mine at Ryddarhyttan in Sweden.

Orthite (allanite, bodenite, cerine, muromontite, pyrorthite, tautolite, uralorthite, wasite), a double silicate of aluminium and the cerium metals (16–25 p.c.), together with smaller quantities of thorium, iron, calcium, and the yttrium metals; found in Greenland, Scandinavia (Arendal, Hitteröe, Stockholm), United States (New York, North Carolina, Pennsylvania, Virginia), Ural Mountains (Miask), and in several localities in Germany.

Monazite (cryptolite, edwarsite, eremite, mengite, turnerite), an orthophosphate of the cerium metals (Ce, La, Nd, Pr)^{III} PO_4, containing 40–70 p.c. of these elements together with varying amounts of thorium (0–18 p.c.); it occurs in the plutonic and older volcanic rocks, and in the alluvial sands of the rivers and coasts of Brazil, North and South Carolina, and Travancore.

Äschynite. A complex, columbate-titanate, containing approximately equal proportions (13–23 p.c.) of thorium and the cerium metals, together with a small proportion of the yttrium group, found at Hitteröe (Norway) and Miask (Ural Mountains).

2. *Minerals containing chiefly Yttrium Earths.*

Ytterbite (gadolinite), a basic silicate containing yttrium earths (40–48 p.c.) and cerium earths (5–10 p.c.), together with glucinum and iron; found in Colorado, Germany (Harz Mountains and Silesia), Scandinavia (Fahlun, Hitteröe, Ytterby), and Texas.

Yttrialite, a silicate of the yttrium metals (43–47 p.c.), thorium (10–12 p.c.), and cerium metals (5–8 p.c.), found in Texas.

Xenotime, a phosphate of the yttrium metals (54–64 p.c.), corresponding with monazite; it contains also smaller amounts of the cerium metals and thorium; found in Brazil, North Carolina, and Norway.

The following minerals contain the yttrium earths and smaller quantities of thoria and the cerium earths united with varying proportions of the more acidic oxides of columbium, tantalum, titanium, tungsten, tin, uranium, silicon, and zirconium.

Fergusonite (bragite, kochelite), found in Ceylon, Greenland, Arendal, Ytterby, Massachusetts, North Carolina, and Texas.

Yttrotantalite, found in Norway, Sweden, and the Ural Mountains.

Samarskite (nohlite, vietinghofite, ytteroilmenite), found in Canada, Connecticut, North Carolina, and Ural Mountains (Miask).

Polycrase, found in Canada, Scandinavia, and North and South Carolina.

Euxenite (loranskite), found in North Carolina, Norway (Hitteröe, Brevig), and Swaziland.

Many other rare complex minerals (fluorides, zircono-silicates, titanates, columbates, tantalates, uranates, &c.) contain considerable amounts of the rare earths, which are also not infrequently found in small quantities in commoner minerals (*e.g.* limestones, apatites, scheelites, &c.). Traces of the rare earth metals have been detected in mineral waters, in the ashes of plants, in urine, and in bone ash.

Extraction of the Rare Earths.—The finely powdered mineral, made into a paste with concentrated sulphuric acid, is heated till the mass becomes dry and hard. The product is extracted with water, the solution treated with hydrogen sulphide to remove copper, bismuth,

molybdenum, &c., and the metals of the rare earths precipitated as oxalates by the addition of oxalic acid. The oxalates are decomposed at 400°, the residual oxides dissolved in dilute sulphuric acid, and the solution saturated with sodium or potassium sulphate, when the double sulphates of the cerium metals are precipitated, whilst those of the yttrium metals remain dissolved.

The complex minerals containing columbium, tantalum, titanium, &c., may be decomposed by hydrofluoric acid, when the foregoing elements form soluble fluorides, whilst the fluorides of the rare earth metals are precipitated. Or these minerals may be broken up by heating with strong sulphuric acid or potassium hydrogen sulphate and the rare earths precipitated by ammonia from the solution of their sulphates. These hydrated oxides are freed from the co-precipitated columbium, tantalum, and titanium hydroxides by prolonged boiling with nitric acid, when the latter hydroxides separate in an insoluble form. The rare earths are precipitated as oxalates from their solution in nitric acid, the oxalates ignited, and the resulting oxides subjected again to the nitric acid treatment until a complete separation is effected.

The methods of separating and purifying the rare earths, which will be further described under the appropriate headings (*v.* CERIUM, YTTRIUM; TERBIUM; THORIUM, &c.) may be divided into the following two classes:—

1. Separations based on differences of basicity.

a. The fractional precipitation of the earths with bases of varying strengths: ammonia, caustic alkalis, magnesium hydroxide, organic bases.

b. The fractional decomposition by heat of the solid nitrates and other salts.

2. Separations based on differences of solubility.

Considerable ingenuity has been shown in separating the metals of the rare earths by taking advantage of the slight differences of solubility exhibited by their salts with acids of widely different types. The following series does not exhaust the list of compounds which have been utilised in these intricate separations: Sulphates, double sulphates, nitrates, double nitrates, chromates, bromates, formates, oxalates, succinates, ethyl-sulphates, acetyl-acetonates, and sulphanilates.

The progress of these separations is followed by chemical and spectroscopic methods.

1. The chemical control consists in determining the equivalent of any fraction either by a gravimetric analysis of its sulphate (Krüss, Zeitsch. anorg. Chem. 1893, 3, 44; Wild, *ibid.* 1904, 38, 191; Brill, *ibid.* 1908, 47, 464; Jones, *ibid.* 1903, 36, 92; Brauner and Pavliček, Chem. Soc. Trans. 1902, 81, 1243), or by a volumetric analysis of its oxalate (Feit and Przibylla, Zeitsch. anorg. Chem. 1905, 43, 202).

2. The most convenient spectroscopic controls are (i.) the *absorption spectra*, exhibited by solutions of the salts of many rare earths (*e.g.* neodymium, praseodymium, samarium, terbium, erbium, thulium, dysprosium and europium); (ii.) the *arc spectra*, in which all the rare earths give characteristic lines both in the visible and ultra-violet regions of the spectrum. Carbon electrodes are employed, the lower one containing a hollow in which is placed the salt under examination. The arc spectra are photographed and the lines identified by comparison with the photograph of an iron spectrum taken under similar conditions. The method is extremely sensitive, although not equally so for different elements (*cf.* SPECTRUM ANALYSIS, and *v.* Exner and Hascheck, Die Wellenlängen der Bogenspektra, 1904; and Hagenbach and Konen, Atlas der Emissionspektren der meisten Elemente, 1905). Other emission spectra (the flame, spark, and cathode luminescence spectra) have been found to give useful indications in certain cases (Crookes, Phil. Trans. 1883, 174, [3] 891; Proc. Roy. Soc. 1885, 38, 414; 1886, 40, 77, 236, 502; Chem. News, 1886, 54, 39, 54, 63, 76, 155; 55, 83, 95; 56, 59, 62, 72, 81; Chem. Soc. Trans. 1889, 55, 255; Proc. Roy. Soc. 1899, 65, 237; Lecoq de Boisbaudran, Compt. rend. 1885, 100, 1437; 101, 552, 588; 1886, 102, 153, 899, 1536; 103, 113, 627; 1887, 105, 258, 301, 343, 784; 1890, 110, 24, 67; Bettendorf, Annalen, 1892, 270, 376; Baur and Marc, Ber. 1901, 34, 2460).

PHYSICAL AND CHEMICAL PROPERTIES OF THE RARE EARTHS AND THEIR MORE IMPORTANT COMPOUNDS.

Oxides and hydroxides. The metals of the rare earths were formerly supposed to be diads (*cf.* Wyrouboff, Bull. Soc. chim. 1889, [3] 2, 745; 1899, [3] 21, 118; Compt. rend. 1899, 128, 1573), but they are now regarded as tervalent elements forming oxides of the type R_2O_3, although cerium, neodymium, praseodymium, and terbium are capable of yielding higher oxides. The more stable oxides of thorium and zirconium are of the form RO_2. The present view of the valency of the metals of the rare earths is supported by the following facts:—

(i.) The isomorphism of bismuth nitrate and certain nitrates of the rare earth series (Bodman, Ber. 1898, 31, 1237).

(ii.) The cryoscopic and ebullioscopic determination of the molecular weights of the chlorides and acetylacetonates (Ber. 1898, 31, 1829; Compt. rend. 1901, 133, 289; Annalen, 1904, 331, 334); these salts are thus found to have the general formula RX_3.

(iii.) The electrical conductivity of the chlorides and sulphates in aqueous solution (Zeitsch. physikal. Chem. 1899, 30, 193; Amer. Chem. J. 1898, 20, 606).

(iv.) The specific heats of cerium, lanthanum and didymium (Annalen, 1873, 168, 45; Ber. 1881, 2821; Bull. Soc. chim. 1882, [2] 38, 139).

The rare earth oxides vary considerably in basic power, lanthana, praseodymia, neodymia, and ceria, Ce_2O_3, being the strongest; whilst neoytterbia, lutecia, scandia, and cerium dioxide are among the weakest bases of the series. In general, the oxides (R_2O_3) of the cerium metals are stronger bases than those of the yttrium group.

The hydroxides are thrown out of solution as gelatinous precipitates by ammonia, ammonium sulphide, and the caustic alkalis, even in the presence of ammonium salts; but this precipitation is prevented by citric or tartaric acid (except in the case of scandium). Unlike thorium and zirconium, the metals of the cerium, terbium, and yttrium groups are not

precipitated as hydrated peroxides from neutral solutions by hydrogen peroxide, but their peroxides separate from alkaline solutions (Brauner, Ber. 1881, 14, 1944; Cleve, Bull. Soc. chim. 1885, [2] 43, 53). These peroxides are very unstable, evolving oxygen even at the ordinary temperature; they are completely destroyed by acids (*v.* CERIUM; *cf.* Melikoff and Pissarjewski, Zeitsch. anorg. Chem. 1899, 21, 70).

Chlorides. The chlorides of the rare earth metals are deliquescent salts readily soluble in water or alcohol, and crystallising from the former solvent with 6 or 7 molecular proportions of water. The anhydrous chlorides, which are fusible at red heat, but very slightly volatile, are obtained either by evaporating their solutions to dryness with ammonium chloride, by heating the corresponding oxides with carbon in a stream of chlorine, or preferably by heating the oxide or dry sulphate in a current of chlorine and sulphur chloride (Matignon and Bourion, Compt. rend. 1901, 133, 289; 1902, 134, 657, 1308; 1904, 138, 631; 1905, 140, 1181; Muthmann and Stützel, Ber. 1899, 32, 3413; Petterson, Zeitsch. anorg. Chem. 1893, 4, 1).

The chlorides of the rare earth metals combine additively with ammonia and organic bases (*e.g.* pyridine; *cf.* Compt. rend. 1905, 140, 141; J. Amer. Chem. Soc. 1902, 24, 540; 1903, 25, 1128; Ber. 1902, 35, 2622), and exhibit a great tendency to form double salts with the less electropositive metals. The platinichlorides of the cerium metals are isomorphous and crystallise in regular octahedra (Ber. 1876, 1722; Annalen, 1878, 191, 331).

Fluorides. The rare earth metals, including thorium, are precipitated completely as gelatinous fluorides by soluble fluorides and by hydrofluoric and fluosilicic acids, in this respect differing from zirconium, which forms a soluble double fluoride.

Nitrates. The nitrates of the rare earths dissolve readily in water or alcohol, those of the cerium group crystallising with 6 molecular proportions of water, whilst the corresponding salts of the yttrium group contain 3–6 molecules of water. The cerium metals readily furnish stable crystallisable double nitrates with the univalent and bivalent metals (ammonium, sodium, magnesium, &c.).

Sulphates. The rare earths dissolve in dilute sulphuric acid, and the solutions deposit hydrated sulphates containing frequently 4, 8, or 12 molecules of water. The octahydrated sulphates of praseodymium, neodymium, yttrium, gadolinium, and ytterbium are isomorphous (monoclinic); but the cerous salt $Ce_2(SO_4)_3.8H_2O$ is rhombic. With excess of acid, the normal sulphates of the rare earths are converted into acid sulphates of considerable stability (Bull. Soc. chim. 1889, [3] 2, 745; Compt. rend. 1902, 134, 657; Zeitsch. anorg. Chem. 1904, 38, 322; Chem. Soc. Trans. 1902, 81, 1243).

The sulphates of the rare earths have the characteristic property of combining with the alkali sulphates; the double sulphates of the cerium group are only sparingly soluble in concentrated solutions of the alkali salts, whilst those of the yttrium group are readily soluble. The double sulphates of the terbium group occupy an intermediate position, being moderately soluble in solutions of alkali sulphates.

Carbonates. Ammonium, sodium, and potassium carbonates precipitate the neutral or basic carbonates from solutions of the rare earths; but these precipitates are soluble in excess of the reagents, and from the solutions thus obtained, crystalline double carbonates are deposited on evaporation. The carbonates of the yttrium metals are generally more soluble than those of the cerium group in solutions of the alkali carbonates.

Oxalates. The rare earth oxalates are precipitated by oxalic acid or soluble oxalates in neutral or acid solutions, and the sparing solubility of these compounds in acids is a characteristic property which serves to separate the rare earths from other metallic bases (Ber. 1898, 31, 1718; 1899, 32, 409).

The oxalates of the rare earths proper dissolve only slightly in ammonium oxalate, differing in this respect from the oxalates of thorium and zirconium, the latter being also soluble in free oxalic acid (Chem. Soc. Trans. 1898, 73, 951). Aqueous ammonium acetate dissolves the oxalates of the yttrium group (Bull. Soc. chim. 1896, [3] 15, 338).

Acetates. The acetates of the cerium group are very soluble and crystallise with difficulty; those of the yttrium group are less soluble. Boiling with sodium acetate precipitates zirconium and thorium from solutions of their soluble salts, but not the rare earths proper, excepting cerium from ceric salts (Ber. 1902, 35, 672).

Formates. The formates of the cerium group are less soluble than those of the yttrium group. These salts have proved useful in separating the elements of the terbium group.

Acetylacetonates. Acetylacetone furnishes well-crystallised salts with the rare earths, and the fractionation of these compounds from alcohol has served in the separation of the yttrium group (Urbain, Compt. rend. 1897, 124, 618; Bull. Soc. chim. 1897, [3] 17, 98; Ann. Chim. Phys. 1900, [7] 19, 184; Biltz, Annalen, 1904, 331, 60; Zeitsch. anorg. Chem. 1904, 40, 218; Hantzsch and Desch, Annalen, 1902, 323, 26).

The Metals of the Rare Earths.—The oxides of the rare earths are very refractory substances, which have not been reduced directly; the metals are generally set free from the anhydrous chlorides. This reduction may be effected with sodium or potassium, but is preferably carried out electrolytically. The dry chlorides, mixed with a small proportion of alkali chloride, or barium chloride, are electrolysed in a copper crucible, fitted with carbon electrodes, the electrolysis being carried out with a current of 30–40 amperes and 12–15 volts. The mixed metal collects in a molten state round the cathode, which passes through the bottom of the crucible. The anode is movable, so that the resistance and therefore the temperature can be increased until all the separated metal melts together. A yield of 750 grams of metal can be obtained with a current of 120 amperes in 6 hours.

With the mixed chlorides, prepared from the waste oxides of the thoria manufacture, the product is the so-called 'mischmetal' (Ce, 45 p.c.; La, Nd, Pr, 35 p.c.; Sm, Er, Gd, Y, 20 p.c.), which has been used, like aluminium in the Goldschmidt

process ('thermite'), to effect the reduction of the refractory oxides of molybdenum, vanadium, columbium, and tantalum (Muthmann, Hofer, and Weiss, Annalen, 1902, 320, 331; 1904, 331, 1; 1905, 337, 370).

Bibliography of the Rare Earths.—Böhm, Darstellung der seltenen Erden; Browning, Introduction to the Rarer Elements; Abegg, Handbuch der Anorganischen Chemie, vol. iii, part i.; Herzfeld and Korn, Chemie der seltenen Erden; Wyrouboff and Verneuil, La Chimie des Terres Rares. G. T. M.

CEROSILINE *v.* WAXES.

CEROTIC ACID $C_{25}H_{51}\cdot COOH$ is found free in beeswax, of which it is the chief constituent (Brodie); as a ceryl ether in Chinese wax and in opium wax (Hesse); and has been obtained from paraffin by oxidation with chromic acid (Marie, Ann. Chem. Phys. [7] 7, 160; Henriques, Ber. 1897, 1418); m.p. 77·5° (M.), 82·5° (H.).

CEROTINE-ORANGE, -PONCEAU, -SCARLETS, -YELLOW *v.* AZO- COLOURING MATTERS.

CEROXYLIN *v.* WAXES; also RESINS.

CERULEÏN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

CERUSSITE. Native lead carbonate ($PbCO_3$), of some importance as an ore of lead (Pb, 77·5 p.c.), being known as white lead-ore. It crystallises in the orthorhombic system and is isomorphous with aragonite ($CaCO_3$) and witherite ($BaCO_3$). Six-rayed stellate groups of twinned crystals are extremely characteristic. The crystals possess an adamantine lustre, are very heavy (sp.gr. 6·5), and effervesce with dilute acid; they are very brittle, breaking with a bright conchoidal fracture; hardness, 3–3½. The mineral occurs in the upper oxidised zones of veins of lead ore, having been formed by the action of carbonated surface waters on galena. Enormous deposits of cerussite intermixed with embolite (silver chloro-bromide) and iodyrite (silver iodide) have been extensively mined at Broken Hill in New South Wales, where little or none of the oxidised ore now remains. Intimately mixed with hemimorphite (hydrated zinc silicate), it is abundant at Broken Hill in North-Western Rhodesia. At both of these localities, many finely crystallised specimens have been found. L. J. S.

CERYL ALCOHOL *v.* WAXES.

CETINE *v.* WAXES.

CETOSAN. Trade name for a mixture of the higher alcohols of spermaceti, mainly cetyl and octodecyl alcohols, with vaseline. When shaken with water, it forms a permanent creamy emulsion (Blatz, J. Soc. Chem. Ind. 1908, 865).

CETYL ALCOHOL, CETYLIC ACID and **CETYL-ACETIC ACID** (*v.* SPERMACETI).

CETYLMALONIC ACID, $CH_3(CH_2)_{14}CH(CO_2H)_2$. Prepared from α-cyanstearic acid and potash (Hell and Sadomsky, Ber. 1891, 2781), or diethylmalonic ester, methyl iodide, and cetyl iodide (Guthzeit, Annalen, 206, 357); m.p. 121·5°–122°.

CEVADINE *v.* VEGETO- ALKALOIDS.

CEYLON MOSS *v.* ALGÆ.

CHAGRAL GUM *v.* GUMS.

CHAILLETIA TOXICARIA (Don.). A plant found in Upper Guinea, Sierra Leone, and Senegambia, the seeds of which contain a poisonous resin used for killing rats and other animals (Power and Tutin, J. Amer. Chem. Soc. 1906, 28, 1170).

CHALCANTHITE. Native copper sulphate, $CuSO_4,7H_2O$, found as a bright-blue efflorescence, or rarely as distinct crystals, in many copper mines, being especially abundant in some of the Chilian mines. In solution it is always present in the waters issuing from copper-mines; these are allowed to flow over scrap iron, the copper being precipitated as cement-copper. About 100 tons of copper have been so saved annually from the waters of the Rio Tinto mine in Spain, and considerable amounts were formerly obtained from the mine waters in Co. Wicklow. L. J. S.

CHALCEDONY *v.* AGATE and QUARTZ.

CHALCOCITE. *Cuprous sulphide* (*v.* COPPER).

CHALCOTRICHITE. Native cuprous oxide (*v.* CUPRITE).

CHALK. A white or greyish, loosely coherent kind of limestone rock, composed almost entirely of the calcareous remains of minute marine organisms (foraminifera, coccoliths, &c.) and fragments of shells. The purest kinds contain up to 99 p.c. of calcium carbonate in the form of the mineral calcite. Silica is always present in small amounts as the mineral opal, representing the remains of other minute marine organisms (radiolaria, &c.) and sponge spicules. Minute grains of quartz, felspar, zircon, rutile, and other minerals are also often present. With the admixture of clayey material there may be an insensible gradation from pure chalk to *chalk-marl* (*v.* MARL). In *phosphatic chalk*, there is much calcium phosphate (up to 45 p.c.); in green *glauconitic chalk* there is an admixture of grains of glauconite (a hydrated iron potassium silicate); and in *red chalk* there is some iron hydroxide. Not only may there be considerable variations in the composition of chalk, but there may also be wide variations in the colour (snow-white, grey, &c.,) and texture of the material. It may be soft, incoherent, and porous, or quite hard and crystalline (as the chalk of the Yorkshire coast).

The uses of chalk are numerous. For example, as a writing material in form of white and coloured crayons; for the manufacture of quicklime, mortar, Portland cement, plaster, &c., and as a fertiliser. Whiting is prepared by grinding chalk and collecting the finer sediments from water; this is used for polishing, making putty, and many other purposes. Under the name of 'Paris white,' chalk is used in the manufacture of india-rubber goods, oilcloth, wall-paper, &c. The harder kinds are extensively used as a building stone.

Large quantities of chalk are quarried in the counties of Kent, Surrey, Sussex, Cambridge, Lincoln, and Hampshire; Kent being by far the most important. The production of English chalk is not far short of five million tons per annum. A certain amount of this is exported to the United States, though there are extensive beds of chalk in Kansas and Texas. (On the English chalk, *see* A. J. Jukes-Browne, The Cretaceous Rocks of Britain, Mem. Geological Survey, 1903.) L. J. S.

CHALK, FRENCH. Steatite or soapstone.

CHALYBITE. Native iron carbonate, $FeCO_3$, forming rhombohedral crystals isomorphous with calcite ($CaCO_3$), and of importance as an ore of iron. It is often known as

siderite, but this name had earlier been applied to two other mineral species, and it is also used as a group name for meteoric irons. Sp.gr. 3·9; hardness, 3½. Small, brilliant crystals of varying habit are common in many mineral veins, for example, those of Cornwall. Veins of massive sparry material showing cleavage surfaces (*Spathic iron-ore*) are mined in the Brendon Hills in Somersetshire, and in Weardale, Co. Durham. The fresh, unaltered material is creamy white in colour ('white ore'), but when slightly weathered it is brown ('brown ore'). The Cleveland ore is a pisolitic form of chalybite occurring as beds in the Lias strata; and the important *clay-iron-stone* and *black-band iron-stone* of the Coal-measures consist of compact chalybite, intermixed with clay and carbonaceous matter. A nodular form with an internal radiated structure is known as *sphærosiderite*.

L. J. S.

CHAMOMILE OIL *v.* OILS, ESSENTIAL.

CHAMOTTE. A mixture of fire clay and burnt pottery used for making fire bricks, crucibles, pipes, &c.

CHARCOAL *v.* CARBON and FUEL.

CHARICIC ACID, CHAVICIN *v. Pepper resin*, art. RESINS.

CHARTREUSE. A famous liqueur formerly prepared at the head-quarters of the Carthusian monks near Grenoble, but now, since the retreat of the monks from France in 1906, made at Tarragona in Spain.

The recipe for the original liqueur or 'elixir vitæ' as it was called, was given by the Marquess d'Estrées to the Carthusian monks of Paris in 1602, but, owing to the difficulty of procuring the necessary alpine plants, they presented it to their brethren of the Grande Chartreuse in 1735.

The *elixir vitæ* was valued as a stimulant for the less robust members of the fraternity, weakened by age or by the privations and hardships entailed by the severity of their religious exercises, and was also dispensed to the feeble poor of the district.

After numerous disasters by fire, pillage, and confiscation of their property through religious and political persecutions, culminating in the loss of everything during the French Revolution, the monastery of La Grande Chartreuse was restored in 1816, although in a very impoverished condition.

The secret of the manufacture of the 'elixir' had, however, been carefully preserved, and this was made the basis of other varieties of liqueur, by the sale of which the monks hoped to improve their finances. The result was the production of green, yellow, and white 'chartreuse,' the virtues of which were advertised far and wide by the military officers who had been quartered in the monastery about the middle of last century. Extensive and modern plant was installed at Fourvoisie in 1863, and, in course of time, the sale of chartreuse increased the revenue of the monastery to a point it had never reached before.

After the passing of the French Religious Associations Act, in 1906, the monks of the Grande Chartreuse migrated across the border to Tarragona in Spain, carrying their secret formulæ with them.

More than 200 ingredients are said to be used in the manufacture of genuine chartreuse, and its spirit basis is rectified grape spirit distilled from sound wine. The usual alcoholic strength of the three varieties of chartreuse is: *green*, 55° of alcohol, or 96 p.c. of proof spirit; *yellow*, 42·5° alcohol, or 74·5 p.c. proof spirit; and *white*, 30° alcohol or 52·5 p.c. of proof spirit.

There are innumerable imitations of chartreuse, mostly prepared from plain spirit flavoured with essential oils and coloured by means of the various ingredients described under CORDIALS AND LIQUEURS. The following formulæ are amongst the best of those suggested for the preparation of imitation chartreuse:—

Ingredients	Green	Yellow	White
China cinnamon	15 grams	15 grams	125 grams
Mace	15 „	15 „	30 „
Lemon balm, dried	500 „	250 „	250 „
Hyssop (flower tops)	250 „	125 „	135 „
Peppermint (dried)	250 „	—	—
Thyme	30 „	—	—
Balsime (*Bal. major*)	125 „	—	—
Genepi	250 „	125 „	125 „
Arnica (flowers)	10 „	15 „	—
Balsam poplar (buds)	15 „	—	—
Angelica (seeds)	125 „	125 „	125 „
Angelica (roots)	62·5 „	30 „	30 „
Coriander	—	1500 „	—
Cloves	—	15 „	30 „
Aloes (Socotrine)	—	30 „	—
Cardamom (small)	—	50 „	30 „
Nutmegs	—	—	15 „
Calamus	—	—	300 „
Tonka beans	—	—	15 „
Alcohol at 85°	62·5 litres	42·5 litres	52·5 litres
White sugar	25·0 kilos.	25·0 kilos.	37·5 kilos.

Digest in the alcohol for 24 hours, distil until nearly all the spirit is over, and dilute to 100 litres. Colour green or yellow as described under CORDIALS AND LIQUEURS, add the sugar, allow to

rest till clear, and filter. (*Sec* CORDIALS AND LIQUEURS.) J. C.

CHAULMOOGRA OIL GROUP. This group is remarkable on account of the considerable optical activity which these oils exhibit, owing to the presence of the strongly active chaulmoogric and hydnocarpic acids (discovered by Power and his collaborators). Hitherto, three oils belonging to this class have been described, viz. *Chaulmoogra oil*, obtained from the seeds of *Taraktogenos Kurzii* (King); *Hydnocarpus oil*, obtained from the seeds of *Hydnocarpus Wightiana* (Blume); and *Lukrabo oil*, the fat obtained from *Hydnocarpus anthelmintica* (Pierre). The saponification values of these oils lie between 204 and 213, and their iodine values between 90 and 86·4. The seeds of Taraktogenos contain a cyanogenetic glucoside. Chaulmoogra is chiefly used in the treatment of leprosy and various skin diseases in Indo-China, Siam, and to some extent also in Europe. Recently chaulmoogra oil has been imported on the Continent as 'Cardamom oil' and used in margarine with disastrous results. J. L.

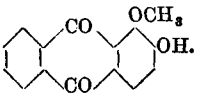
CHAY ROOT. Chay root or Chay aver (from *chaya*=which fixes colours, and *ver*=root); also called Indian madder, is the root of *Oldenlandia umbellata* (Linn.), Rubiaceæ. It bears the following Indian vernacular names: turbuli (*Bengali*); cheri-vello (*Telugu*); ché or chay, sayawer, imburel (*Tamil*). The plant is a small bush or herb found on sandy soils, chiefly near the sea-coast. It occurs in North Burma and Ceylon, but is most abundant in certain tracts of the Madras Presidency, from Orissa southward. It does not appear to be used in Bengal, but on the Malabar and Coromandel coasts, especially the latter, it is extensively cultivated, and employed in dyeing a colour analogous to Turkey-red. The chief market is Madras, where it is sold in small bundles at about 4*d.* a lb. The roots are usually about 10–12 ins. long and ¼ in. thick, somewhat straight and stiff, tough and wiry, and with few or no lateral fibres. When freshly gathered, they have an orange colour; but when dried and kept, they assume a yellowish-grey hue. Boiling water gives merely a pale-yellow extract, but if alkali is added, a blood-red decoction is soon obtained. The colouring principles seem to reside chiefly, if not entirely, in the bark of the root.

The literature connected with chay root is extremely meagre, and is for the most part contained in the following publications: *Philosophy* of Permanent Colours, 2, 282, 1813, Bancroft; Bulletin de la Société industrielle de Mulhouse, 5, 302, 1832, E. Schwartz and D. Koechlin; L'Art de la Teinture des Laines, 475, 1849, Gonfreville. Quantities of the root were imported into Europe in 1774 and at later periods, and its dyeing properties were examined by the above-mentioned experts. It met with little practical success, however, as it was not found to possess any advantage over madder; indeed, it was considered to have but one-half or even a fourth of the colouring power of madder; further, it was found to contain certain undefined yellow substances of an acid character, which interfered somewhat with its dyeing power. Still, it was recognised as a good dyestuff, giving the usual madder colours, and equally fast to soap. It is evident that the yellow substances referred to are not the same as those described in this article, as Schwartz states that they were present in larger quantity in 'nona' (*Morinda citrifolia*) than in chay root, whereas these yellow substances exist in much larger quantity in chay root than in morinda root. Very probably they refer to Rochleder's 'rubichloric acid,' as this is contained in morinda root in larger amount than in chay root. Schützenberger, in his Traité des Matières colorantes, 2, 291, 1867, states that he found chay root to contain alizarin and chlorogenin (rubichloric acid) and that it was easy to exhaust the root by extraction with alcohol.

In many respects chay root resembles madder, as both contain ruberythric acid, alizarin, rubichloric acid, and cane sugar, but there are very marked differences in the nature of the other constituents of the two roots. Madder, as is well known, contains purpurin, purpurin- and purpuroxanthin-carboxylic acids, &c., and but traces of yellow crystalline substances, forming barium compounds soluble in water, which have not been at all fully investigated. In chay root the former substances are entirely absent, but, on the other hand, although the root contains considerable quantities of yellow crystalline substances, they are quite distinct from those contained in madder.

The phenolic constituents of this root have been studied by means of the sulphurous acid extraction method described in detail in connection with MADDER, and also by a subsequent exhaustion of the residual root with boiling lime water. In this manner, chlororubine, alizarin, and a mixture of non-tinctorial yellow substances were isolated. These latter are present in chay root (probably as glucoside) in comparatively large amount (1 p.c.), and have been shown to consist principally, if not entirely, of the following substances.

Alizarin α-methylether crystallises from dilute methyl alcohol in long orange-yellow needles, melting at 178°–179°. It has the constitution

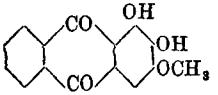


This interesting compound has not as yet been synthetically produced from alizarin, all attempts in this direction having resulted in the formation of the corresponding β-methoxy-derivative. The methoxyl group present in this substance is much more readily hydrolysed than is usually the case, for prolonged digestion with boiling baryta water is sufficient for this purpose, a precipitate consisting of barium alizarate thus separating. This property, therefore, accounts for the difficulty in obtaining either this compound or alizarin dimethylether by means of methyl iodide, for in this process of methylation a prolonged digestion in the presence of free alkali is necessary. On the other hand, whereas alizarin is only converted with considerable difficulty into alizarin dimethylether, by the action of methyl sulphate, alizarin α-methylether readily yields this substance when treated with this reagent in the usual manner.

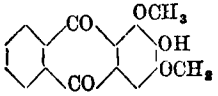
Acetyl alizarin α-methylether crystallises in yellow needles, melting at 212°.

Anthragallol dimethylether (A) forms yellow

needles, melting at 209°, and dissolves in alkaline solutions with a red colouration. It is distinguished from the isomeric compound described below, in that it yields an ammonium salt, crystallising in scarlet prisms, which is sparingly soluble in cold alcohol. Heated with sulphuric acid to 180°, or with hydrochloric acid, it is converted into anthragallol, and when methylated by means of methyl sulphate, is readily converted into anthragallol trimethylether. By the action of 10 p.c. potassium hydroxide in a sealed tube at 180° for 5 hours, it is partially converted into methoxyalizarin:

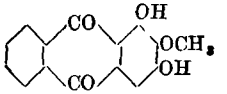


and a similar reaction occurs when sulphuric acid at 100° is employed. The constitution assigned to this anthragallol dimethylether (A), is therefore as follows:—

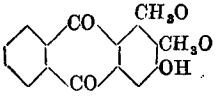


Acetylanthragallol dimethylether crystallises in pale-yellow prisms, melting at 213°–215°.

Anthragallol dimethylether crystallises in yellow leaflets, melting at 230°–232°, and gives a red ammonium salt which is soluble in cold alcohol. Heated with 10 p.c. potassium hydroxide solution to 180° for 5 hours, it is partially converted into a compound having the reactions of methoxypurpuroxanthin



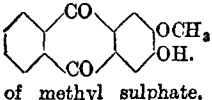
and with little doubt possesses the following constitution:—



By methylation with methyl sulphate in the usual manner, this compound is readily converted into anthragallol trimethylether.

Acetylanthragallol dimethylether (B) consists of long yellow needles, melting at 176°–178°.

Hystazarine monomethylether obtained as long orange-yellow needles, melting at 232°, when heated with hydrochloric acid at 180°, is converted into hystazarine. Alkaline solutions dissolve it with a crimson colouration, and its ammonium and potassium salts which crystallise in garnet-red needles are insoluble in cold *iso*butylic alcohol. The constitution of hystazarine monomethylether is as follows:—



By means of methyl sulphate, it yields hystazarine dimethylether, which consists of yellow glistening needles, melting at 235°–236°.

Metahydroxyanthraquinone, pale-yellow needles, melting at 302°, probably identical with the well-known artificial compound which is prepared from anthraquinonemonosulphonic acid by digestion with alkali.

Dyeing Properties.—Although chay root contains acid principles which tend to dissolve the mordants, its employment as a dyestuff presents no difficulty. The only precautions necessary to be observed are to add 2 p.c. of chalk to the dye-bath, and to raise the temperature gradually to the boiling-point.

Dyeing experiments on ordinary stripe-printed calico, containing alumina and iron mordants, have shown that the dyeing power of chay root is equivalent to the presence of a percentage of 0·33–0·35 alizarin. Compared with ground madder root of good quality, it seems to have about half its dyeing power when the comparison is made before soaping, but after soaping it appears to be quite equal to madder. The reds, pinks, and chocolates have a distinctly bluer shade than those given by madder, and the lilacs are much fuller and brighter and very similar to those obtained from alizarin. This last feature alone ought to have secured a ready market for chay root among the European dyers, previous to the introduction of artificial alizarin, and it is somewhat strange that its marked suitability for lilacs should have escaped the observation of those who formerly made dyeing experiments with this root.

On oil-prepared calico, mordanted with alumina, chay root gives an excellent blue shade of Turkey-red, withstanding the operation of clearing with soap and stannous chloride better even than a madder dyed red, and quite equal to one obtained by means of artificial alizarin. Good brown, red, orange, and purple colours are readily obtained on wool, and also on silk, suitably mordanted with chromium, aluminium, tin, and iron, according to the ordinary method usual with dyers. On wool, the colours not being submitted to any soaping operation, chay root appears to possess about half the dyeing power of madder.

Boiled with dilute sulphuric acid, chay root yields a 'garancine' of a very dark-green colour and possessing about three times the dyeing power of the original root.

Literature.—A. G. Perkin and J. J. Hummel Chem. Soc. Trans. 1893, 63, 1160; *ibid.* 1895, 817; A. G. Perkin (*ibid.* 1907, 91, 2066); J. J. Hummel and A. G. Perkin (J. Soc. Chem. Ind. 1894, 13, 346). A. G. P.

CHEDDITE. An explosive consisting of a mixture of ammonium perchlorate, dinitrotoluene and castor oil (*v.* Explosives).

CHEESE. A solid preparation of the casein from milk, together with the fat and some of the other constituents so prepared as to encourage the action of certain ferments which make it more digestible and palatable.

Cheeses may be made from the milk of various animals, but they are usually prepared from that of the cow, which is either used in its natural condition, or may be first divided into cream and separated milk, from both of which products cheeses are also made.

In the case of cream cheeses, the lactic acid produced by the lactic ferments may be used for thickening the cream; but in the majority of cheeses, rennet is used to precipitate the casein. The caseinogen of the milk is converted into casein by the rennet ferment, and this, in the

presence of the lime salts of the milk, is followed by the separation of insoluble calcium caseinate or curd, which carries with it nearly all the fat, some of the other constituents of the milk, and the enzymes of the rennet and milk. This curd differs from that produced by acids, which throw out caseinogen from the combinations with lime in which it occurs in milk.

The mechanical condition of the rennet curd, used for making different cheeses, is controlled by the acidity of the milk and by the temperature of renneting. If milk is curdled with rennet without the previous development of acidity, a soft curd results; this curd will not shrink so much as a curd produced from an acid milk. Too much acidity, on the other hand, results in a hard curd, which will shrink to a much greater extent, giving a hard 'acid' curd.

Temperature also exerts an important influence in cheese making; the action of the rennet is hastened up to about 100°F., and ceases at about 130°F. The temperature employed, the degree of acidity, and the quantity of rennet used, will vary with different cheeses and also with the nature of the milk, the ash constituents probably exerting a considerable influence. The acidity is often controlled by the addition of 'starters,' *i.e.* pure cultures of suitable lactic ferments or of mixed cultures in milk or whey, to the milk. The average temperature used is about 84°F., at which the coagulation takes some 40 to 60 minutes. In some cheeses, *e.g.* Leicester, Dutch cheeses, &c., annatto is added as colouring matter at least 10 minutes before the rennet. Salt is also added at various stages in the manufacture, in the case of hard pressed cheese, when the curd has been ground prior to being put in the mould for pressing into shape; in the case of soft cheese, about the time it is fit to take out of the mould.

With hard-pressed cheeses such as Cheddar, Cheshire, Derby, Leicester, Gloucester, Ementhaler, Gruyère, and Edam, the curd is cut up by means of a curd knife or apparatus of wire meshes, it is then stirred and heated to acquire the correct stage of dryness, consistency, and acidity, after which the whey is drawn off and the curd allowed to remain till a certain degree of acidity has developed. This is tested for with a hot iron against which the curd is pressed, the length of the threads which draw out on pulling away the curd being taken as an index of the acidity produced; the percentage of acidity at the various stages of manufacture may accurately be determined by means of the acidimeter. The curd is then ground in a mill, and afterwards pressed in a mould into a shape which varies with the different cheeses. After being pressed for 2 or 3 days, the cheese is ripened in a curing room, the humidity and temperature of which should be under control; a temperature of about 55 to 65°F. being most generally desirable.

To another group of cheeses, in which the process of manufacture varies considerably from the above, belong the moulded cheeses, in making which the pressing process is omitted, or in the case of Wensleydale greatly reduced; the resulting cheese being softer and admitting of the growth of blue veins of mould (*Penicillium glaucum*) in the cracks left between the pieces of curd which extend throughout the cheese. To this group belong Stilton, Roquefort, Gorgonzola, Wensleydale, &c.

In the case of the small 'soft' cheeses of the Camembert type, considerable variations are made in the process of manufacture, the resulting cheese being quickly ripened by moulds, or rather by the enzymes produced by moulds, which grow on the outside of the cheeses. *Penicillium candidum* and *Oidium Lactis* play an important part in the ripening of Camembert.

The chemical analysis of cheese includes the determinations of the water, fat, total nitrogen, ash, and salt. The products of ripening are also sometimes determined, and the fat may be examined for adulteration with animal fats.

To determine the water, ash, and salt, 2 or 3 grams of well-sampled cheese, cut into small pieces, are weighed into a flat-bottomed dish and placed in the water-bath at 100°C., the dish being inclined so that the fat runs off the drying curd. Weighings are made every hour, and the water is found to have all been driven off in about 5 or 6 hours.

The melted fat is then poured off and the residue well macerated in hot amyl alcohol; the residue may be then burnt and the ash weighed, the salt being afterwards dissolved out with water and the solution titrated with N/10 silver nitrate.

Ether may be used to extract the fat, and the dried curd and fat afterwards weighed; but a better method is to take a fresh portion of 3 or 4 grams of the cheese and grind with twice its weight of anhydrous copper sulphate in a small mortar, afterwards extracting with ether in a Soxhlet extractor.

Modifications of the Werner-Schmid or Göttlieb-Rose methods also give good results.

The total nitrogen is determined by the Kjeldahl method in about 1 gram of cheese.

According to Richmond, the products of ripening may be determined in the following manner: 10 grams of the cheese are placed in a small mortar and ground up with 25 c.c. of boiling water; the liquid is then decanted through a filter into a 250 c.c. flask, the process being repeated with nine further similar measures of boiling distilled water. The total filtrates are then cooled, made up to the 250 c.c. mark, and well mixed. The products of ripening are determined by the evaporation in a dish of an aliquot part (50 c.c.); this, after drying till constant at 100°C., is afterwards burnt, the weight of the dish and ash being subtracted from the weight of the dish and dry residue. The difference between 100 and the sum of the water, fat, ash, and products of ripening, may be taken as unaltered casein.

The primary products of ripening may be determined in another 50 c.c. of the filtrate by the Ritthausen method as follows: 5 c.c. of copper sulphate solution are added and the solution neutralised with caustic soda solution; the precipitate which forms is collected in a weighed Gooch crucible; it is then washed well and dried in a water-oven, the fat is then extracted with ether, and the residue dried till constant. The crucible and its contents are then ignited and weighed, the difference giving the weight of the primary products of ripening, *i.e.* soluble proteins, &c.

To examine the fat, about 50 grams are dried

till the fat runs out: the remaining fat is then extracted from the residue with ether, the ether evaporated and the fat examined, as in the case of butter fat. The soluble and insoluble acids and the Reichert-Wollney figure being generally determined, the addition of animal fats can be thus detected. The removal of fat from milk used in making cheese can be assumed if the fat is less than 45 p.c. of the dried cheese or less than six times the total nitrogen.

Composition of Cheese (Bell).

Description	100 parts contain					Proportion of fat in 100 parts of dry cheese	Proportion of fat in 100 parts of casein and fat	Salt per cent. in cheese	Percentage composition of fat.	
	Water	Fat	Casein or nitrogenous matter	Free acid as lactic	Ash				Soluble acids	Insoluble acids
Stilton	23·57	39·13	32·55	1·24	3·51	51·19	52·50	0·67	4·42	88·96
American (red)	28·63	38·24	29·64	—	4·49	53·57	52·12	0·72	4·26	89·66
American (pale)	31·55	35·93	28·83	0·27	3·42	52·49	53·34	0·82	4·81	88·49
Roquefort	32·26	34·38	27·16	1·32	4·88	50·75	54·24	3·04	4·91	88·70
Gorgonzola	31·85	34·34	27·88	1·35	4·58	20·39	53·08	2·11	4·40	89·18
Cheddar (medium)	35·60	31·57	28·16	0·45	4·22	49·02	50·49	1·43	4·55	88·75
Gruyère	33·66	30·69	30·67	0·27	4·71	46·26	47·07	0·81	4·41	88·97
Cheshire	37·11	30·68	26·93	0·86	4·42	48·78	50·84	1·69	5·55	87·76
Single Gloster	35·75	28·35	31·10	0·31	4·49	44·12	45·24	1·28	6·68	86·89
Dutch	41·30	22·78	28·25	0·57	7·10	38·80	42·41	4·45	5·84	87·58

The ripening process in cheese, whereby it usually acquires a more agreeable flavour, is essentially a fermentation of slow character, which is brought about by micro-organisms which are generally present in the milk or in the air of the dairy. They can only be controlled, to a limited extent, by the process of making, temperature, &c. It is not possible to destroy undesirable organisms by sterilisation, for heated milk will not make typical cheese as far as is at present known, though heating to 130°F. is now sometimes practised for soft cheeses. Cleanliness, from the moment the milk leaves the cow, is of the utmost importance.

The organisms which cause most trouble to the cheese maker are those which produce gas, which, when it develops in the curd, produces what is known as heaving or blown cheeses. These organisms, to which *Bacillus coli commune* belongs, often come from manure. Their absence can be demonstrated by what is known as a fermentation test, which consists in placing about 10 c.c. of the milk in a sterile test-tube and keeping it at blood heat for about 18 hours, after which time no signs of bubbles of gas should be seen in the tube.

Bitterness in cheese is sometimes caused by bacteria, as is the case when the milk is infected with *Micrococcus casei amari* or *Tyrothrix geniculatus*. An interesting example of a bitter cheese organism is that of *Torula amara*, which, after causing much trouble and loss in Canada, was eventually traced to the leaves of the sugar maple, from which source it infected the clean churns which were stood under the trees after being cleaned.

Black spots in cheese may be caused by moulds or by particles of iron which get into the milk and are afterwards changed to sulphide by the sulphuretted hydrogen produced in ripening. Other organisms which produce colours (moulds, &c.), may get into the milk or may be derived from the air or utensils of the dairy at later stages of the manufacture.

The cheese maggot is the larva of the fly *Piophila casei*; the cheese mite is *Tyroglyphus* (Lafr.) *siro*.

It must be remembered that micro-organisms and the enzymes they produce play a most important part in ripening; how far this process is also dependent on the proteolytic enzymes of the rennet and to the natural enzymes of the milk is not yet fully ascertained. As above mentioned, pure cultures of lactic acid organisms are sometimes added to milk to be used for hard-cheese making, and Camembert is often infected with the appropriate mould. Gorgonzola is also sometimes infected with mould to make the desired blue veins. As a general rule, however, the dairy and district where a particular kind of cheese is made contain the organisms which are necessary for the successful manufacture of the cheese in question.

Oleomargarine and Lard Cheese. The success attending the sale of margarine as a substitute for butter has led manufacturers, especially in America, to introduce foreign fats of animal or vegetable origin in the production of cheese as a means of utilising skim-milk; the cream which has been abstracted being replaced by lard, oleomargarine, and by cotton-seed oil.

Analyses of Oleomargarine and Lard Cheeses (Bell).

—	100 parts of cheese contain				Per cent. of salt	100 parts of fat contain		Melting-point of fat
	Water	Fat	Casein and free acids	Ash		Insoluble fatty acids	Soluble fatty acids	
Oleomargarine	30·95	28·80	36·27	3·98	1·14	92·43	2·16	77°F.
Lard	31·30	24·66	38·87	5·17	1·55	92·88	1·55	92°F.

In flavour and character these samples closely resembled milk-fat cheese. Comparison of the results of the analysis of the two samples with those yielded by genuine cheeses in the former table conclusively proves the admixture with foreign fat. The low percentage of soluble acids indicates that more than one-half of the fat has not been derived from milk. J. G.

CHEIROLINE. An alkaloid obtained from the seeds of the wallflower (*Cheiranthus cheiri*), where it occurs to the extent of 1·6–1·7 p.c. and probably as a glucoside. *Cheiroline*, $C_5H_9O_2NS_2$, forms colourless prisms, $a:b:c=0{\cdot}9418:1:0{\cdot}6228$; m.p. 47°–48°; b.p. 200°/3 mm.; it is an optically inactive neutral substance, and is similar to quinine in its physiological action; it is readily hydrolysed by cold dilute sodium hydroxide, yielding carbon dioxide, hydrogen sulphide, and a *basic substance* $C_4H_{11}O_2NS$, according to the equation

$$C_5H_9O_2NS_2+2H_2O=C_4H_{11}O_2NS+CO_2+H_2S.$$

The *hydrochloride* of the base, $C_4H_{12}O_2NSCl$ forms deliquescent prismatic crystals, m.p. 145°–146°, and the *quaternary methiodide* $C_7H_{18}O_2NIS$ crystallises in silky scales m.p. 183° (Wagner, Chem. Zeit. 1908, 32, 76; Schneider, Ber. 1908, 41, 4466; 1909, 43, 3416).

The base is identical with *methyl-γ-amino-propylsulphone* $SO_2Me(C_2H_4)\cdot CH_2\cdot NH_2$, prepared synthetically from *methyl-γ-phthaliminopropyl-sulphide*, and is converted by Hofmann's method with carbon disulphide into *cheiroline*, which is therefore a methylsulphone derivative of propylthiocarbimide $SO_2Me\cdot CH_2\cdot CH_2\cdot CH_2\cdot NCS$ (Schneider, Annalen, 1910, 375, 207).

CHEMICAL AFFINITY. There has been much fruitless speculation about chemical affinity, about the nature of the force which impels two different substances to react with one another. During the last half-century, however, the efforts of physical chemists have been devoted rather to the practical investigation of the way in which chemical affinity manifests itself, and of the extent to which the operation of this force is modified by altering the external conditions. Quantitative methods have been devised for studying the influence of concentration, of temperature and pressure, and of foreign substances, on the course and products of a reaction. The object of this article is to give an outline of the methods employed and the results obtained in this study of the operation of chemical affinity. The three chief divisions into which the discussion of the subject naturally falls are (1) velocity of chemical reactions; (2) chemical equilibrium; (3) catalysis.

Velocity of chemical reactions. It is well known that different chemical reactions proceed to completion at very different rates. One change may be so rapid as to be practically instantaneous, whilst in another case the reacting substances may appear almost indifferent to each other. The rate of chemical change depends, however, to a marked extent on the temperature, so that the velocity of a reaction which takes place with extreme rapidity is moderated on lowering the temperature, and becomes amenable to experimental investigation. Suppose now that for such a reaction as that represented by the equation A+B=C+D, a range of temperature has been found over which the change proceeds at a measurable rate; the question next arises, How is the velocity of the change, at a given temperature, dependent on the quantities of the reacting substances A and B? In dealing with this question, we shall assume that the reaction system is homogeneous, and that the change proceeds completely from left to right, *i.e.* until either A or B has disappeared.

The reaction system being homogeneous, it is permissible to regard matters from the molecular-kinetic point of view, and to conceive the interaction of the substances A and B as taking place only in so far as the molecules of A come in contact with the molecules of B. The velocity of the reaction, therefore—that is, the rate at which A and B disappear—will be proportional to the frequency of the collisions between a molecule of A and a molecule of B, even although only a certain proportion of the collisions is followed by chemical interaction. Now, on kinetic grounds, the frequency of the collisions between molecules of A and B is proportional to the product of their concentrations, hence the velocity of reaction between A and B is proportional to the product of their concentrations (or their 'active masses,' as it is sometimes put). This proposition is nothing else than the law of mass action, applied to the chemical change under consideration.

The foregoing proposition may be formulated in more definite shape. If a is the concentration of the substance A, and b is the concentration of the substance B at the beginning of the reaction, then the initial velocity of the change, V_0, is given by the equation $V_0=k_1 . ab$, where k_1 is a proportionality factor, the numerical value of which is independent of the concentrations of the reacting substances, and varies only with temperature and other external conditions. If, now, the reaction is allowed to proceed for an interval of time t, and if x represents the extent to which the concentrations of A and B have been diminished by the progress of the change, then the velocity at time t, V_t, is given by the equation $V_t=k_1 . (a-x)(b-x)$. It is obvious that V_t must be less than V_0, and that the velocity of the reaction must diminish continuously from the start onwards: V_t, therefore, represents the velocity of the reaction only for an infinitely short space of time. This velocity is defined by the rate at which x is, at that moment, increasing with the time, and if, using the language of the differential calculus, we indicate by dx the extent to which x increases in the infinitely short space of time dt, we may write $V_t=\frac{dx}{dt}=k_1 . (a-x)(b-x)$.

The applicability of the law of mass action, as expressed in the foregoing formula, is best appreciated by reference to a particular case, such as the inversion of sucrose. Although this change, which may be represented by the equation $C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$, takes place with appreciable velocity only in the presence of a catalytic agent such as hydrochloric acid, yet the latter is found unaltered when the reaction is over, and the inversion of sucrose may be regarded as a particular case of the reaction A+B=C+D. The fact that the inversion is carried out in aqueous solution permits, however, a simplification of the formula

$\frac{dx}{dt}=k_1.(a-x)(b-x)$; the water taking part in the reaction is a small fraction of the total water present, so that x may be neglected in comparison with b, and we may write $\frac{dx}{dt}=k(a-x)$, where $k=k_1.b$. Integration of this equation leads to the formula $k=\frac{1}{t}.\log_e\frac{a}{a-x}$, in which, as already indicated, a is the initial concentration of sucrose, and $a-x$ is its concentration after the inversion has proceeded for t units of time.

In order to test the validity of the formula $k=\frac{1}{t}.\log_e\frac{a}{a-x}$ as applied to the inversion of sucrose, it is only necessary to ascertain the amount of sucrose still present in the reaction mixture at intervals during the progress of the inversion, and then to see whether the amount of sucrose varies with the time in the manner required by the formula. The simplest way of following the course of sugar inversion is to use the polarimeter. The reaction mixture, that is, sucrose solution containing a catalytic agent such as hydrochloric acid, is put in the polarimeter tube, which should be provided with a water-jacket in order to secure a constant temperature during the progress of the inversion. The angle of rotation is determined at the beginning of the change, at subsequent intervals, and finally when the change is complete. If we indicate by α_0, α, and α_∞, the initial angle of rotation, the angle at time t from the start, and the final angle respectively, then $\alpha_0-\alpha_\infty$ is a measure of a, the total sucrose undergoing inversion, and $\alpha-\alpha_\infty$ is similarly a measure of $a-x$, the sucrose which has still to undergo inversion after time t. Hence $\frac{a}{a-x}=\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}$ and the formula which should represent the course of the inversion becomes $k=\frac{1}{t}.\log_e\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}$. From the ascertained values of t, α_0, α, and α_∞, it is easy to discover whether the expression on the right-hand side of the equation is constant or not. The experimental data recorded in the following table show how far in a particular case the actual course of sucrose inversion corresponds with the velocity formula:—

Inversion of Sucrose at 25° by N/2 HCl.

t in minutes	Angle of rotation	$k=\frac{1}{t}.\log_{10}\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}$
0	+25·16°	—
56	16·95°	0·00218
116	10·38°	0·00218
176	5·46°	0·00219
236	1·85°	0·00219
371	−3·28°	0·00221
∞	−8·38°	—

The expression evaluated in the last column is $\frac{1}{t}.\log_{10}\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}$ instead of $\frac{1}{t}.\log_e\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}$, but, obviously, if the value of the former expression is constant, the value of the latter must be so also. The figures in the last column are satisfactorily constant, and the figure 0·00219 may therefore be taken as the velocity coefficient for the inversion of sucrose under the specified conditions, viz. at 25° and in presence of N/2 HCl. The variation of the velocity coefficient with temperature and with the concentration of the acid will be discussed later.

Reactions, in which only one molecule of a single substance undergoes change, are termed *unimolecular* reactions, or reactions *of the first order*. The course of all such reactions, apart from possible disturbing factors, is represented by the formula $k=\frac{1}{t}.\log_e\frac{a}{a-x}$. Examples of strictly unimolecular changes, to which the foregoing formula has been found applicable, are the transformation of acetochloranilide into *p*-chloroacetanilide, the Beckmann rearrangement, and the decomposition of nickel carbonyl. The inversion of sucrose is, strictly speaking, not a unimolecular but a bimolecular reaction, for both water molecules and sugar molecules are involved in the change. The reaction takes place, however, in aqueous solution, and, as already indicated, the consequence is that the course of the inversion conforms to that characteristic of a strictly unimolecular change. In many other similar cases, a bimolecular reaction proceeds in accordance with the formula $k=\frac{1}{t}.\log_e\frac{a}{a-x}$. Examples of this are the hydrolysis of methyl acetate and the decomposition of diazo- salts.

It is desirable here to emphasise certain features which are characteristic of unimolecular reactions, features which can indeed be read out of the velocity formula, but are most clearly seen by the consideration of experimental data. In the first place, for all unimolecular reactions the amount of change occurring in a given interval of time is a constant fraction of the unchanged substance still present. This is a necessary consequence of the fundamental velocity equation, as is clear when it is written in the form $\frac{dx}{a-x}=kdt$, but the proposition is also in harmony with observation, as will be seen by a consideration of the following data bearing on the inversion of sucrose (Armstrong and Caldwell, Proc. Roy. Soc. A. 1905, 74, 199). A sucrose solution was inverted at 20° with hydrochloric acid, and the angle of rotation (α) was determined from time to time, with the results shown below:

Time	α
0	+21·55°
15	20·40°
120	13·75°
135	12·95°
225	8·62°
240	8·02°
∞	−7·18°

The decrease in rotation during the first 15 minutes, viz. 1·15°, is a measure of the amount of change during that interval. The average rotation of the solution over this interval may be taken as $\frac{21·55°+20·40°}{2}=20·97°$, and a measure of the unchanged sucrose present is given by 20·97+7·18=28·15. The ratio of the amount of change occurring in the first 15 minutes to the amount of unchanged sucrose present is therefore $\frac{1·15}{28·15}=0·041$. If now the intervals from 120 to 135 minutes, and from 225 to 240 minutes are similarly considered, it will be found that the ratio of the amount of change occurring in the 15-minute interval to the amount of unchanged sucrose present is 0·039 in each case, practically the same value as for the first 15 minutes of the inversion. The

experimental data, therefore, bear out the statement that for a unimolecular reaction the amount of change occurring in a given interval of time is a constant fraction of the unchanged substance still present.

Another feature of unimolecular reactions is that the amount of substance changed in a given time is always the same *fraction* of the total amount of substance present at the beginning of the reaction, however this latter amount be varied. An illustration of this is furnished by the following data, referring to the inversion of sucrose in very dilute aqueous solution under the influence of invertase:—

Grams sucrose per 100 c.c.	Grams sucrose inverted in 60 mins.
1·00	0·249
0·50	0·129
0·25	0·060

This experimental result is implied in the formula for a unimolecular reaction, for if $y=\frac{x}{a}$ is the fraction of the total sucrose which has been inverted up to time t, the formula may be written $k=\frac{1}{t}\cdot\log_e\frac{1}{1-y}$, and it is plain that the value of y depends merely on t, and is independent of a.

For bimolecular reactions, that is, reactions in which two molecules are concerned, the fundamental velocity equation is $\frac{dx}{dt}=k(a-x)(b-x)$, as indicated in the argument above. Integration of this equation leads to the formula $k=\frac{1}{(a-b)t}\cdot\log_e\frac{b(a-x)}{a(b-x)}$. If, however, the two reacting substances have the same initial concentration, that is, if $a=b$, the integrated formula is $k=\frac{1}{t}\cdot\frac{x}{a(a-x)}$.

A typical case of a bimolecular reaction, or reaction of the second order, is the saponification of an ester by an alkali. Under suitable conditions of temperature and concentration, the velocity of saponification is measurable, and the progress of the reaction can be determined by extracting samples of the reaction mixture from time to time and titrating for free alkali. The figures in the following table, referring to the saponification of ethyl acetate by sodium hydroxide at 24·7°, will serve to show how far the experimental data are in harmony with the formula just recorded. The reaction mixture in this case was N/40 in relation both to ester and alkali, and the figures under $a-x$ in the table are the volumes of a standard acid solution required to neutralise 10 c.c. of the reaction mixture:—

t (min.)	$a-x$	$ka=\frac{1}{t}\cdot\frac{x}{a-x}$
0	8·04	—
4	5·30	0·129
6	4·58	0·126
8	3·91	0·132
10	3·51	0·129
12	3·12	0·131
15	2·74	0·129
20	2·22	0·131

The figures in the last column are satisfactorily constant, and confirm the application of the law of mass action to a bimolecular reaction.

Reactions of the third and higher orders are known and the formulæ applicable to these are obtained on the lines already indicated. Cases of such reactions, however, are comparatively rare, and it is not proposed to discuss them here. Investigation has shown that frequently a reaction which a general knowledge of the facts would lead us to regard as a reaction of a high order turns out to be one of a low order. This result is undoubtedly due to the apparently complex reaction being really a series of successive changes of a simpler kind. Under these circumstances, the velocity of the complex reaction is determined by those of the component reactions which are comparatively slow. If, for instance, one of the latter is incomparably slower than all the others, then the order of the complex reaction will be the order of this slow component reaction.

Influence of Temperature.—It is well known that a chemical reaction is markedly accelerated by even a slight rise of temperature, but a definite measure of the influence of temperature on a given reaction can be obtained only by determining the velocity coefficient of the reaction at different temperatures. The value of the temperature coefficient of reaction velocity, deduced in this way, is remarkably independent of the nature of the particular reaction under investigation. For homogeneous reactions of the most varied character, the factor by which the velocity coefficient at T° must be multiplied in order to give the velocity coefficient at T+10°, lies, as a rule, between 2 and 4. Speaking generally, one may say that the velocity of a chemical reaction is doubled or trebled for every rise of 10°. It is a striking fact that the temperature coefficient of various vital processes, such as vegetable respiration, is of the same order as that found for chemical reactions generally.

Chemical equilibrium. The reactions discussed in the foregoing section have all been changes which proceed from left to right until at least one of the reacting substances has disappeared. There are many reactions, however, which do not belong to this type, inasmuch as they come to a stop while the reacting substances are still present in the reaction mixture. Suppose, for instance, that the reaction between two substances A and B is of this description, and that C and D are the products of the reaction; then the change proceeds until a state of equilibrium is attained at which all four substances are present. It is further found that if the products C and D are brought together, they react to form the substances A and B, while the final state of equilibrium reached is the same as in the previous case. Such a reaction is known as a *balanced* or *reversible* reaction, and in the corresponding equation a double arrow is substituted for the usual sign of equality; thus: $A+B\rightleftarrows C+D$.

The progress of a reversible reaction towards its equilibrium position may be regarded as the resultant of two opposed velocities, one the velocity (v_1) with which the substances on the left side react to form those on the right side of the equation, and the other the velocity (v_2) with which the substances on the right side react to form those on the left side of the equation. If we take $A+B\rightleftarrows C+D$ to represent the

reversible reaction in question, and suppose that at some particular moment the concentrations of the four substances in the reaction mixture are a, b, c, and d respectively, then at that moment $v_1=k_1ab$ and $v_2=k_2cd$. The observed velocity of the change is, of course, the difference between v_1 and v_2. If now the change has proceeded at constant temperature until the equilibrium position is reached, and the concentrations of the four substances are a_e, b_e, c_e, and d_e respectively, then $v_1=k_1a_eb_e$, and $v_2=k_2c_ed_e$. Since there is equilibrium, the forward reaction is exactly balanced by the back reaction, so that $v_1=v_2$ and $k_1a_eb_e=k_2c_ed_e$, or $\frac{k_1}{k_2}=\frac{c_e\cdot d_e}{a_e\cdot b_e}$. If the ratio $\frac{k_1}{k_2}$ is replaced by the one constant K, we have $K=\frac{c_e\cdot d_e}{a_e\cdot b_e}$. K is known as the *equilibrium constant*, and its numerical value defines the relationship which must exist between the equilibrium concentrations of the substances involved in a reversible reaction. The argument employed above might obviously be extended to reversible reactions other than $A+B\rightleftarrows C+D$: the result in all cases would be an equilibrium formula involving a constant ratio between the product of the equilibrium concentrations of the substances on the right side and the product of the equilibrium concentrations of the substances on the left side, however the values of these concentrations might vary individually. It ought, perhaps, to be pointed out here that, in the equilibrium formula, the concentration of any substance, n molecules of which take part in the reaction, must be raised to the nth power.

In discussing the application of the law of mass action to reversible reactions with the help of the equilibrium formula, we shall deal first with cases in which the reaction system is homogeneous. As an example, the equilibrium between carbon dioxide, hydrogen, carbon monoxide, and water vapour may be considered; the reaction in question is represented by the equation $CO_2+H_2\rightleftarrows CO+H_2O$, and is obviously of the type $A+B\rightleftarrows C+D$. In Hahn's investigation of this equilibrium (Zeitsch. physikal. Chem. 1903, 44, 513), platinum was used as a catalytic agent, and on this ground the objection might be raised that the reaction as studied by that investigator is not really homogeneous. A true catalytic agent, however, as will be shown in greater detail at a later stage, does not affect the position of equilibrium in a reversible reaction, but merely lessens the time required for the attainment of equilibrium. The reaction which takes place between carbon dioxide and hydrogen, or between carbon monoxide and water vapour in contact with platinum, may therefore be regarded as a homogeneous reaction. In Hahn's experiments, mixtures of the gases were passed through a heated quartz or porcelain tube containing spongy platinum. Provided that the rate of passage was slow enough to allow the four gases to come into equilibrium with each other, analysis of the issuing gas gave the equilibrium concentrations, C_{CO_2}, C_{H_2}, C_{CO}, and C_{H_2O}. The relationship between these required by the law of mass action is $K=\frac{C_{CO}\cdot C_{H_2O}}{C_{CO_2}\cdot C_{H_2}}$, and the validity of the law in the case of this reaction is shown by the fact that the value of K obtained is, for a given temperature, the same when carbon dioxide and hydrogen, in varying proportions, are allowed to react, as when carbon monoxide and water vapour are taken as the initial substances. A few figures obtained by Hahn at 986° will serve to support this statement. Mixtures of carbon dioxide and hydrogen, in the proportions shown in the following table, were passed through the reaction vessel, and from analysis of the issuing gas the values of K were calculated by the above formula.

Initial mixture		Equilibrium mixture			
CO_2	H_2	CO_2	$CO=H_2O$	H_2	K
10·1	89·9	0·70	9·46	80·38	1·59
30·1	69·9	7·18	23·00	46·82	1·58
49·1	51·9	21·36	27·88	22·88	1·59
60·9	39·1	34·20	26·61	12·58	1·64
70·3	29·7	47·66	22·79	6·76	1·61

Experiments were made, also at 986°, in which the initial mixture contained carbon monoxide and water vapour: the mean value of K, deduced from these experiments, was 1·55, slightly lower than the average of the figures recorded in the table. The discrepancy, however, is not great, and the numerical data quoted suffice to show that the balance established between the four gases, whatever be their initial concentrations, is adequately defined by the mass action formula.

A reversible reaction of great technical importance is the one which forms the basis of the sulphuric acid contact process:

$$2SO_2+O_2\rightleftarrows 2SO_3$$

and consideration of this case from the standpoint of the mass action law throws light on many points connected with the process. The reaction may be regarded as a homogeneous one, for the catalysts used in the technical process do not affect the final balance between the gases, but only accelerate the attainment of equilibrium.

The application of the law of mass action, in this case, leads to the result $\frac{C^2_{SO_3}}{C^2_{SO_2}\cdot C_{O_2}}=\text{const.}$, in which C_{SO_3}, C_{SO_2}, and C_{O_2} are the equilibrium concentrations of the respective substances. It is convenient, however, to work with the reciprocal of the foregoing expression, and to regard the equilibrium constant as defined by $K=\frac{C^2_{SO_2}\cdot C_{O_2}}{C^2_{SO_3}}$. The accuracy of this formula may be tested with the help of the experimental data obtained by Bodenstein and Pohl (Zeitsch. Elektrochem. 1905, 11, 373). These investigators passed a mixture of sulphur dioxide and oxygen over spongy platinum, contained in heated quartz tubes, and determined the equilibrium concentrations by analysing the issuing gas. The figures in the following table, obtained at 727°, show that the value of K, worked out from the equilibrium concentrations, is independent (1) of the relative proportions of sulphur dioxide and oxygen passed into the apparatus, (2) of the presence or absence of nitrogen:—

Initial gas ratio $2SO_2$: O_2 : N_2	$K \times 10^3$
0·21 : 1 : 0	3·49
0·62 : 1 : 0	3·59
1·20 : 1 : 0	3·48
1·68 : 1 : 0	3·51
3·97 : 1 : 0	3·67
1·23 : 1 : 3·76	3·60
1·31 : 1 : 3·76	3·54
1·55 : 1 : 3·76	3·52

The experiments showed also that the value of K obtained for a particular gas mixture was independent (1) of the direction in which the equilibrium position was approached, (2) of the rate at which the gaseous mixture was passed over the catalyst. The latter result is the guarantee that the equilibrium position was really attained.

Similar results were obtained at various other temperatures, and it was found that the value of K increased rapidly with rising temperature, as shown by the following figures:—

Temp. C.	$K \times 10^3$
528°	0·015
579°	0·077
627°	0·32
680°	1·12
727°	3·54
789°	12·6
832°	28·0
897°	81·6

This increase means that, as the temperature rises, the position of equilibrium is shifted in favour of the system $2SO_2+O_2$; in other words, the dissociation of sulphur trioxide becomes greater. For each set of conditions, the extent of the dissociation is defined by the corresponding numerical value of K, deduced from a formula based on the foregoing table. It is possible, then, for a given temperature and given proportions of sulphur dioxide, oxygen and nitrogen in the initial gaseous mixture, to calculate what will be the relative quantities of trioxide and dioxide in the equilibrium mixture, that is, to calculate the 'yield' obtainable. The results of such calculations for various proportions of the gases and for various temperatures, are embodied in the following table. The numbers recorded in the last four columns are the percentages of sulphur dioxide convertible into sulphur trioxide under the specified conditions:—

Initial gaseous mixture SO_2	O_2	N_2	400°	500°	600°	700°
10·1 p.c.	5·05 p.c.	84·85 p.c.	96·2	83·2	59·1	31·9
7·0	10·0	83·0	99·3	93·4	73·3	42·5
4·0	14·6	81·4	99·4	94·9	78·3	48·1
2·0	18·0	80·0	99·5	95·6	80·5	51·3

These figures bring out clearly one other point involved in the equilibrium formula, namely, the influence of the partial pressure of the oxygen. If the equilibrium formula is written in the form

$$\frac{C^2_{SO_3}}{C^2_{SO_2}} = \frac{1}{K} \cdot C_{O_2} \quad \text{or} \quad \frac{C_{SO_3}}{C_{SO_2}} = \frac{1}{\sqrt{K}} \cdot \sqrt{C_{O_2}},$$

it is plain that the yield at a given temperature can be raised by increasing the partial pressure of the oxygen, and this conclusion is borne out by the foregoing table. The figures show also that the lower the temperature the better is the yield, but it must be remembered that from the technical point of view the time necessary for the attainment of equilibrium is also an important consideration. Fortunately, with platinum as catalyst, the union of sulphur dioxide and oxygen takes place with satisfactory rapidity, even at temperatures as low as 400°–500°, at which the dissociation of the trioxide is comparatively slight. With less active catalysts, however, such as ferric oxide, a higher temperature is required to secure a satisfactory velocity of reaction, and this involves a reduction of the obtainable yield.

Many other dissociation equilibria, similar in type to the case just discussed, have been successfully attacked from the standpoint of the law of mass action. One instance is the equilibrium $N_2O_4 \rightleftarrows 2NO_2$, a case in which a physical method, namely, the determination of the vapour density, must be employed to find the relative proportions of the reacting substances in the equilibrium mixture. Obviously, no direct chemical method of analysis is permissible in any case where the equilibrium shifts rapidly at the *ordinary* temperature, for such analysis involves the removal of one of the substances involved, and this at once upsets the equilibrium.

Another technically important reaction, studied from the standpoint of the mass action law, is that which forms the basis of the Deacon process (*see* von Falckenstein, Zeitsch. physikal. Chem. 1907, 59, 313; 1909, 65, 371). When a mixture of hydrogen chloride and air is passed through a heated chamber containing bricks impregnated with cupric chloride, the hydrogen chloride and oxygen react, producing chlorine and water vapour, but the reaction comes to a stop before all the hydrogen chloride disappears; the reaction, in fact, is a reversible one, and may be represented thus:

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O.$$

Experiments have shown that the equilibrium is defined by an equilibrium constant

$$K = \frac{C^2_{Cl_2} \cdot C^2_{H_2O}}{C^4_{HCl} \cdot C_{O_2}}$$

the value of which, at a given temperature, is the same, whether the initial gaseous mixture taken is hydrogen chloride and oxygen (air) or chlorine and water vapour. The value of K diminishes as the temperature rises, hence the extent to which hydrogen chloride can be converted into chlorine also diminishes with rising temperature. If x represents the fraction of hydrogen chloride convertible into chlorine, then the value of x can be calculated for any given temperature from the corresponding value of K and the partial pressure of the oxygen. For a dry mixture of 76·1 p.c. HCl and 23·9 p.c. O_2, the value of x is 0·865 at 352°, 0·79 at 430°, and 0·55 at 650°. If air is substituted for oxygen so that the ratio of hydrogen chloride and oxygen remains the same, the value of x is 0·71 at 430°. This is approximately the temperature employed in the technical process, and the yield obtained is about 70 p.c. The use of lower temperatures, which would increase the yield, is precluded practically because of the much longer time required for the attainment of equilibrium.

The cases of equilibrium discussed so far have been those in which gases alone are involved. There are, however, many homogeneous reversible reactions in which liquid or dissolved substances take part. A classical example is the reaction between ethyl alcohol and acetic acid, represented thus:

$CH_3{\cdot}COOH + C_2H_5OH \rightleftarrows CH_3{\cdot}COOC_2H_5 + H_2O$.

If 1 mol. of acid and 1 mol. of alcohol are heated in a sealed tube at 100° for a sufficient time, examination of the reaction mixture shows that it contains $\frac{1}{3}$ mol. each of acid and alcohol, and $\frac{2}{3}$ mol. each of ester and water. If then 1 mol. of ester and 1 mol. of water are mixed and treated in the same way, the equilibrium mixture finally obtained has the same composition as in the first case. The reaction therefore is truly reversible and the equilibrium constant is given by the equation $K=\frac{C_e \cdot C_w}{C_{ac} \cdot C_{al}}$, where C_e, C_w, C_{ac}, and C_{al} are the equilibrium concentrations of the four substances. If v represents the volume of the equilibrium mixture in litres, then for the case where 1 mol. each of acid and alcohol are taken initially $C_e = C_w = \frac{\frac{2}{3}}{v}$ and $C_{ac} = C_{al} = \frac{\frac{1}{3}}{v}$, whence $K=4$. It should be pointed out that the composition of the equilibrium mixture may safely be determined by titrating the free acetic acid, for the velocity of the reaction between ethyl alcohol and acetic acid is negligibly small at ordinary temperatures.

If the law of mass action is strictly applicable to the reaction under consideration, then the value of K obtained in experiments in which alcohol and acid are taken in other than molecular proportions should also be 4. Suppose, for instance, that m mols. of alcohol are allowed to act on 1 mol. of acid, and that after equilibrium has been reached, the fraction x of a mol. of ester has been produced; then $C_e = C_w = \frac{x}{v}$, $C_{ac} = \frac{1-x}{v}$, and $C_{al} = \frac{m-x}{v}$; so that $K = \frac{x^2}{(1-x)(m-x)}$. Instead of seeing whether the insertion of the known values of m and x in this formula gives the value 4 for K, the applicability of the mass action law may be tested by taking $K=4$, and ascertaining whether the value of x calculated by the formula for a given value of m is in agreement with the value of x determined experimentally. This procedure has been adopted in the actual investigation of the case, with the following results:—

m	x found	x calc.
0·08	0·078	0·078
0·28	0·226	0·232
0·50	0·414	0·423
0·67	0·519	0·528
1·5	0·819	0·785
2·24	0·876	0·864
8·0	0·966	0·945

The excellent agreement of the figures in the second and third columns furnishes a convincing proof of the applicability of the law of mass action. The influence of 'mass' or concentration in affecting equilibrium is very clearly illustrated by the numbers quoted in the table, for it will be observed that when the amount of alcohol is great compared with the amount of acid, the latter is almost quantitatively converted into ester, in other words, the 'yield' of ester from acid is nearly theoretical.

According to a widely accepted view, an electrolyte dissolved in water is dissociated into positively and negatively charged particles, called ions, and investigation of the conductivity of electrolytic solutions and of the abnormal effect of electrolytes on the freezing-point and boiling-point of water supports the contention that the degree of this ionic dissociation increases with the dilution of the solution, and diminishes when the solution becomes more concentrated. The equilibrium, therefore, between the undissociated molecule of an electrolyte and the ions may be regarded as reversible and can be represented thus: $AB \rightleftarrows \bar{A} + \overset{+}{B}$. If this view is correct, then, as Ostwald pointed out, the equilibrium must be governed by the law of mass action, and the relationship between the concentrations of AB, $\bar{A}$, and $\overset{+}{B}$ at a given temperature must be defined by an equilibrium constant. Suppose, for instance, that acetic acid is the electrolyte in question, then the equilibrium is represented by

$$CH_3{\cdot}COOH \rightleftarrows \overline{CH_3{\cdot}COO} + \overset{+}{H},$$

and the equilibrium formula will be $K=\frac{C_1 C_2}{C}$ where C, C_1, and C_2 are the concentrations of the undissociated molecules and of the two ions respectively. Since, however, the ions are produced in equivalent quantities, $C_1 = C_2$ and $K=\frac{C_1^2}{C}$. If we are dealing with a solution containing 1 gram-mol. of acetic acid in V litres of solution, and if we take α to indicate the fractional extent to which the molecules are dissociated, then in V litres there is $1-\alpha$ gram-mol. of undissociated acetic acid, and accordingly $C=\frac{1-\alpha}{V}$. Similarly, $C_1=\frac{\alpha}{V}$, so that $K=\frac{\alpha^2}{(1-\alpha)V}$. For all binary electrolytes which, like acetic acid, dissociate into two ions, exactly the same formula would be obtained. The equation is the algebraic expression of what is known as Ostwald's Dilution Law, and K is usually termed a *dissociation constant* or an *ionisation constant*: it is also called an *affinity constant*.

The determination of α is based on the relationship $\alpha=\frac{\lambda}{\lambda_\infty}$, where λ is the equivalent conductivity of the electrolyte at the dilution V, and λ_∞ is the limiting maximum value of the equivalent conductivity. The application of the law of mass action to the equilibrium between acetic acid and its ions and to other similar cases is justified by the fact that the value of $\frac{\alpha^2}{(1-\alpha)V}$ is independent of the dilution at a given temperature. In support of this statement, the following figures for acetic acid may be quoted:—

V	$K \times 10^6$
16	1·79
32	1·82
64	1·79
128	1·79
256	1·80
512	1·80

An equally satisfactory constancy of the expression $\frac{\alpha^2}{(1-\alpha)V}$ has been observed in the case

of all acids and bases which are dissociated to a comparatively small extent, and for these the validity of Ostwald's Dilution Law may be regarded as established. For some reason, however, which has not yet been adequately explained, highly dissociated electrolytes, such as strong acids and bases and neutral salts, do not obey Ostwald's Dilution Law.

Keeping in view this limitation to the validity of the formula $K = \frac{a^2}{(1-a)V}$, we may ask: What is the significance of the constant K? The answer will be plain if two feebly dissociated acids, HA_1 and HA_2, are compared at the same dilution V. Since the acids are feebly dissociated, it is a very close approximation to the truth to put $1-a_1=1$ and $1-a_2=1$, so that $K_1 = \frac{a_1^2}{V}$ and $K_2 = \frac{a_2^2}{V}$. A comparison of the equations shows that the relative value of the dissociation constants is closely related to the degree of dissociation; to put it generally, the dissociation constant is a measure of the ability of an acid to yield hydrogen ions, which, according to the modern view, are responsible for the characteristic properties of acids. The value of K for an acid is, therefore, a measure of its strength, of its power to manifest those properties which are associated with acids. One set of circumstances in which the relative strength of two acids is an important factor is realised when one gram equivalent of a base, such as sodium hydroxide, is added to a solution containing one gram equivalent of each of the two acids. The base is insufficient to neutralise both acids, and the result is a competition between the two acids, each securing a fraction of the base. A theoretical discussion of this problem shows that if x is the fraction of the base appropriated by the first acid HA_1, and $1-x$ accordingly the fraction appropriated by the other acid HA_2, then $\frac{x}{1-x} = \sqrt{\frac{K_1}{K_2}}$. If, therefore, the values of K_1 and K_2 have been determined in the way already described, it is possible to calculate the distribution of the available base between the two competing acids. That this can be done in good agreement with experiment is shown by the following figures:—

HA_1	HA_2	x calc.	x found
Dichloracetic acid	Lactic acid	0·95	0·91
Formic acid	Acetic acid	0·75	0·76
Acetic acid	Butyric acid	0·54	0·53

It is evident, then, that a knowledge of the dissociation constant of an acid enables us to calculate relatively the *affinity* or *avidity* of this acid for a base. There are other methods for ascertaining the relative affinity or avidity of an acid, methods available in the case of strong acids which do not obey the dilution law, and to which, therefore, no definite value of K can be assigned. Among these methods are the determination of the heat effects accompanying neutralisation (Thomsen), the measurement of the density changes (Ostwald), and the study of the influence of acids in accelerating the inversion of sucrose or the hydrolysis of methyl acetate. The *order* of magnitude of the values obtained by these and other methods for the relative affinity of acids is the same, as will be seen by an inspection of the following table:—

Acid	K × 100	Relative affinity deduced from Sucrose inversion	Relative affinity deduced from Density changes
HCl	—	100	100
HNO_3	—	100	100
$CCl_3 \cdot COOH$	30 (approx.)	75	80
$CHCl_2 \cdot COOH$	5·14	27	33
$CH_2Cl \cdot COOH$	0·155	4·8	7
$H \cdot COOH$	0·021	1·5	3
$CH_3 \cdot COOH$	0·0018	0·4	1

The manner in which a dissociation equilibrium is affected by excess of one of the products of dissociation has already been referred to in connection with the sulphuric acid contact process. It was there shown that as the equilibrium concentration of the oxygen is increased, so the extent to which the sulphur dioxide is converted into trioxide is increased also. In other words, the dissociation of sulphur trioxide into sulphur dioxide and oxygen is diminished in presence of excess of oxygen, one of the products of dissociation. An analogous statement may be made in connection with the electrolytic dissociation of an electrolyte, such as acetic acid. If to a solution of this acid a quantity of $\overline{CH_3 \cdot COO}$ ions is added, the dissociation of the acid is diminished to a large extent, *i.e.* the concentration of the hydrogen ions is very much reduced, and the acid character of the solution almost disappears. It is true that $\overline{CH_3 \cdot COO}$ ions cannot be added by themselves, but a solution of the sodium salt of acetic acid serves the purpose, for such a salt, to judge from its conductivity, is highly dissociated into $\overline{CH_3 \cdot COO}$ ions and sodium ions. That the effective acidity of an acetic acid solution almost disappears on the addition of a little sodium acetate solution is very clearly seen by comparing the effects of (1) the acetic acid solution, (2) the acetic acid solution + sodium acetate, on the inversion of sucrose. It has been found that the velocity of inversion in presence of

$$\frac{N}{4}CH_3 \cdot COOH + \frac{N}{4}CH_3 \cdot COONa$$

in about $\frac{1}{3}$ what it is in presence of $\frac{N}{4}$ CH_3COOH alone. Not only is this influence of a neutral salt on the effective acidity of a weak acid to be expected on the basis of the mass action law, but it has also been found possible, with the help of the equilibrium formula, to calculate accurately the effect produced by adding any given quantity of the neutral salt.

The cases of equilibrium so far discussed have been those which occur in homogeneous systems, but there are numerous cases also of non-homogeneous or heterogeneous equilibrium. The bearing of the law of mass action on reversible reactions of this character will be most readily appreciated by considering one or two examples. The dissociation of calcium carbonate may be taken in the first place. If this substance is heated to 750° in a closed space, it breaks up to some extent into calcium oxide and carbon dioxide: if, on the other hand, carbon dioxide at atmospheric pressure is passed over calcium oxide, heated to the afore-mentioned temperature, the reverse action takes place and calcium carbonate is formed. That is to say, an equilibrium is established which may be

represented t[illegible] $\rightleftarrows CaO + CO_2$. In applying the law of mass action to this case, we are confronted with the question: What is the concentration or 'active mass' of a solid taking part in a reaction? An answer to this question may be reached by supposing that in the gaseous phase of the reaction system there is equilibrium between the calcium carbonate, the calcium oxide, and the carbon dioxide; that is, each of the solid substances concerned in the reaction is supposed to have a definite, if infinitely small, sublimation pressure at a given temperature, and therefore to be represented in the gaseous phase. On this basis, the equilibrium at a given temperature would be governed by the formula $K_1 = \frac{C_2C}{C_1}$, where C_1, C_2, and C are the equilibrium concentrations of calcium carbonate, calcium oxide, and carbon dioxide in the gaseous phase, respectively. If partial pressures are employed instead of concentrations, the formula would be $K = \frac{\pi_2\pi}{\pi_1}$. Now π_1 and π_2, being sublimation pressures, have fixed values at a given temperature, and are independent of the absolute amounts of calcium carbonate and calcium oxide present. Hence $\pi =$ const., and since π_1 and π_2 are negligibly small, π, the partial pressure of the carbon dioxide, is practically equal to p, the total pressure exerted by the system; so that we may write $p =$ const. The application, therefore, of the law of mass action to the dissociation of calcium carbonate leads to the result that at each temperature the reaction system exerts a definite pressure—the dissociation pressure, as it is termed. This statement is valid only on the understanding that the substances involved in the reaction are kept in contact with each other; if provision is made for keeping the pressure of the carbon dioxide permanently below or above the equilibrium value, then a reaction proceeds until the calcium carbonate (in the first case) or the calcium oxide (in the second case) has disappeared. By artificial alteration of the pressure at constant temperature, therefore, any reaction of the same type as $CaCO_3 \rightleftarrows CaO + CO_2$ may be made to proceed either from left to right, or *vice versâ*. The reaction $2BaO_2 \rightleftarrows 2BaO + O_2$ is also a case where two solids and a gas are in equilibrium with each other, and it may be treated in the same way as the dissociation of calcium carbonate.

Perhaps the chief point that emerges from the foregoing is that the active mass of a solid taking part in a chemical reaction is constant. The correctness of this conclusion has been confirmed by the investigation of various heterogeneous reactions different in type from the dissociation of calcium carbonate. One of these may be considered here, viz. the equilibrium represented by $3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$ (*see* Deville, Compt. rend. 1870, 70, 1105, 1201; 71, 30; Preuner, Zeitsch. physikal. Chem. 1904, 47, 385). On the assumption that the active masses of the iron and the iron oxide are constant, the application of the law of mass action obviously leads to the result $\frac{p_{H_2O}}{p_{H_2}} =$ const., p_{H_2O} and p_{H_2} being the partial pressures of the water vapour and the hydrogen when equilibrium has been established at a definite temperature. This relationship is verified by the experimental results, some of which are quoted in the following table. The experiments consisted in exposing iron in an electrically heated closed system to the action of water vapour kept up to a constant pressure (p_{H_2O}). From the total pressure reached at equilibrium—$p_{H_2O} + p_{H_2}$ the partial pressure of the hydrogen could easily be deduced. It was further found that, starting with excess of hydrogen and iron oxide, the equilibrium could be reached in the other direction. The results recorded in the table were obtained at a temperature of 900°; the pressures are given in millimetres of mercury:—

p_{H_2O}	p_{H_2}	$\frac{p_{H_2O}}{p_{H_2}}$
8·8	13·5	0·65
12·7	18·0	0·71
21·5	30·6	0·70
35·0	52·0	0·67
49·3	71·8	0·68

When the [illegible] nature of the experiments is taken into account, the numbers in the last column may be regarded as satisfactorily constant and as demonstrating the applicability of the mass action law to this case. Although in a closed system an equilibrium is reached in the way described, yet if provision is made for removing the hydrogen as fast as it is formed, and thereby keeping its partial pressure permanently below the equilibrium value, the reaction will proceed until the iron is all converted into oxide.

There are many reversible reactions involving a solid substance and a liquid, or a solid and a dissolved substance. Here also the active mass of the solid is constant at a given temperature, solubility and sublimation pressure being analogous quantities. The equilibrium formula undergoes, therefore, a similar simplification to that illustrated in the foregoing paragraphs.

Influence of Temperature.—In general, a reaction system which is in equilibrium at a given temperature is no longer in equilibrium when the temperature is altered. A measure of this influence of temperature on chemical equilibrium is found in the change of the equilibrium constant, and an illustration of the extent to which K may change with temperature has already been given in connection with the oxidation of sulphur dioxide to trioxide. The exact relationship between temperature and equilibrium is defined by a formula associated with the name of van't Hoff, according to which $\frac{d(\log_e K)}{dT} = -\frac{q}{RT^2}$. The symbol K is the equilibrium constant, that is, the ratio between the product of the equilibrium concentrations of the substances on the right side of the equation and the product of the equilibrium concentrations of those on the left side; q is the heat evolved when the reaction goes completely from left to right, T is absolute temperature, and R is the gas constant. The theoretical basis of van't Hoff's formula need not be discussed here, but one or two points involved in it may be indicated. It is evident, in the first place, that when the heat effect of a reversible reaction is small, the

variation in K is also small, *i.e.* the position of equilibrium is but slightly shifted on altering the temperature. An instance of this is furnished by the reversible reaction between ethyl alcohol and acetic acid. Again, if q is positive, $\frac{d(\log K)}{dT}$ is negative, so that K diminishes with rising temperature, corresponding to a shifting of the equilibrium in favour of the substances on the left side of the equation. If, on the other hand, q is negative, $\frac{d(\log K)}{dT}$ is positive, and a rise of temperature, therefore, involves a displacement of the equilibrium in favour of the substances on the right side of the equation. It will be observed that in both cases, whether q is positive or negative, a rise of temperature involves a shifting of the equilibrium in the direction which means absorption of heat.

As an illustration of the applicability of van't Hoff's formula in an individual case, the reaction $2SO_3 \rightleftarrows 2SO_2+O_2$ may be taken. From the values of the equilibrium constant obtained for this reaction at different temperatures (*see* p. 751), the values of q over narrow intervals of temperature were calculated by the formula. It was found that q is a linear function of the temperature, and may, in fact, be represented by the equation $q=-47300+4T$. If this expression for q is inserted in the formula $\frac{d(\log K)}{dT} = -\frac{q}{RT_2}$, and the equation is integrated, the following formula is obtained:—

$$\log_{10} K = -\frac{10378}{T} - 2{\cdot}222 \log_{10} T + 14{\cdot}585.$$

The relation between K and T expressed in this formula is almost exactly that observed in the experimental investigation: this appears from the following figures:—

t° C.	log K found	log K calc.
528	−4·809	−4·817
579	−4·126	−4·099
627	−3·500	−3·502
680	−2·914	−2·893
727	−2·451	−2·453
789	−1·900	−1·922
832	−1·553	−1·573
897	−1·089	−1·083

Catalysis. No discussion of reaction velocity or chemical equilibrium would be complete without a reference to the phenomenon of catalysis. It very frequently happens that a chemical reaction, which of itself is extremely sluggish, proceeds with comparative rapidity in presence of some foreign substance—a *catalyst*, as it is called. Cases of such an acceleration of a chemical reaction have long been known, and in both laboratory and technical processes catalysts are in common use.

A rational quantitative study of catalysis is possible only on the basis of the law of mass action. In the velocity coefficient, as already explained, we have a definite measure of the rate of a chemical change under given conditions. For a given reaction, therefore, which is catalytically accelerated, the value of the velocity coefficient at a given temperature is a measure of the efficiency of the catalyst, and by comparing the values obtained for the velocity coefficient in different experiments, one can find out how the efficiency of a catalyst varies with the conditions under which it works, and how the efficiency of one catalyst compares with that of another working under the same conditions.

General Characteristics of Catalysts.—One very common and striking feature of catalysis is that the quantity of the catalyst is so small compared with the quantities of the main reacting substances. As a rule, too, the activity of the catalyst at the end of the reaction which it has accelerated is unimpaired. An illustration of these features of catalysis is furnished by the influence of colloidal platinum in promoting the union of hydrogen and oxygen at the ordinary temperature. In some experiments made by Bredig, 2·5 c.c. of colloidal platinum solution (containing 0·17 milligram of platinum) were shaken with electrolytic gas, with the following results:—

Time in minutes	Decrease in the volume of gas	Decrease per minute
10	17·8 c.c.	1·78
20	35·8 ,,	1·80
30	54·8 ,,	1·90
40	72·4 ,,	1·76
50	90·2 ,,	1·78

The average of the figures in the last column is a measure of the catalytic efficiency of the colloidal platinum in the early stages of its activity. The same colloidal platinum was then shaken intermittently during 14 days with the mixture of hydrogen and oxygen, about 10 litres of which disappeared in this time. Not only is the contrast between the minute quantity of the catalyst and the extent of the induced change sufficiently striking, but a determination of the actual rate of disappearance of the gas at the end of the 14 days showed that the rate of decrease, measured over successive 10-minute intervals, was 2·02, 1·87, 1·95, 1·97, and 2·01 c.c. per minute. From these figures it is obvious that the catalytic efficiency of the colloidal platinum is unimpaired. In connection with this case, however, the objection might be raised that hydrogen and oxygen do not combine at the ordinary temperature, and that the platinum ought to be regarded, not as accelerating a change which would take place in its absence, but as actually initiating the reaction. The answer is that at 500° hydrogen and oxygen combine with appreciable rapidity in the absence of a catalyst, but that, in view of the large temperature coefficient of reaction velocity, the rate of union naturally becomes insignificant even at 400°, whilst at ordinary temperatures the two gases appear not to react at all. There is, however, no reason to suppose that there is a definite temperature below which absolutely no combination takes place.

The mere fact that the amount of a catalyst may be almost infinitely small compared with the amounts of the substances changed under its influence, shows that the final state of the reactive system must be independent of the catalyst; in particular, if the accelerated reaction is reversible, the state of equilibrium finally attained must be the same as when no catalyst is present. The catalyst, that is, influences only the rate at which the condition of equilibrium is reached, not the position of equilibrium itself. Experimental evidence in favour of this proposition is supplied by Turbaba's

investigation of the relationship between aldehyde and paraldehyde. The conversion of paraldehyde into the equilibrium mixture, which at 50·5° contains 33·9 p.c. aldehyde, is accompanied by an expansion, and the course of the change may therefore be followed by means of a dilatometer. Various substances accelerate the change, but the difference between the initial and final volumes, as shown by the following figures, is independent of the nature and the amount of the catalyst:—

Catalyst	Per cent. of catalyst	Percentage increase of volume
Sulphur dioxide	0·08	8·20
" "	0·07	8·34
" "	0·002	8·19
Zinc sulphate	2·7	8·13
Hydrochloric acid	0·13	8·13
Oxalic acid	0·52	8·27
Phosphoric acid	0·54	8·10

If the position of equilibrium in a reversible reaction is independent of the catalyst, then K, the equilibrium constant, must be similarly independent. Further, since $K = \frac{k_1}{k_2}$, where k_1 and k_2 are the velocity coefficients of the forward and back reactions, it follows that the catalyst must accelerate the forward and the back reaction in the same proportion. This has been demonstrated in connection with the catalytic effect of acids on the action between an acid and an alcohol and the reverse change. It should further be pointed out that the amount of energy transformed during a chemical change, being dependent only on the initial and final states of the system, is independent of the catalyst. The latter may be compared to the oil which facilitates the sliding of a weight down an inclined plane, without affecting the total energy derivable from the fall of the weight.

Another point of great interest is the relationship between the value of the velocity coefficient for a given reaction at a given temperature and the concentration of the catalyst. In many cases the relationship is a linear one. The rate of inversion of sucrose by acids, for instance, is proportional to the concentration of the hydrogen ions, provided that this concentration is low; on the basis of this proportionality, in fact, it is possible to calculate the velocity of inversion by dilute acetic acid from the velocity observed with dilute hydrochloric acid. In other cases, however, the relationship between reaction velocity and concentration of catalyst is not a linear one. The decomposition of hydrogen peroxide under the influence of colloidal platinum is an illustration of this. The course of the decomposition can be followed by extracting a definite volume of the reaction mixture from time to time and titrating with potassium permanganate. The course of the change is in harmony with the formula for a unimolecular reaction, and for each concentration of platinum a definite value of k, the velocity coefficient, can be obtained. The following table contains the values of k corresponding to various concentrations of platinum:—

Platinum concentration	k
$21{\cdot}0\times10^{-6}$	0·072
$10{\cdot}5\times10^{-6}$	0·024
$5{\cdot}2\times10^{-6}$	0·0084
$2{\cdot}6\times10^{-6}$	0·0027

From these figures it appears that when the concentration of the catalyst is doubled, the velocity of decomposition is trebled.

Catalysis and the law of mass action.—The general characteristics of catalysts have been discussed in the foregoing paragraphs, but it must be admitted that the phenomena associated with catalysis are frequently more complex than has been suggested. It appears that the catalyst often works in such a way as to mask the operation of the law of mass action altogether. Although a detailed discussion of these peculiarities of catalytically accelerated reactions is not possible here, a brief consideration of some typical cases will be found useful.

A careful study has been made of the rate at which sulphur dioxide and oxygen unite in presence of platinum (*see* Bodenstein, Zeitsch. physikal. Chem. 1907, 60, 1), and the results show that the velocity of union is independent of the oxygen concentration (except when it is extremely small), proportional to the concentration of sulphur dioxide, and inversely proportional to the square root of the trioxide concentration. This behaviour is obviously quite different from what would be expected under the law of mass action. The most satisfactory explanation seems to be that the factor which really determines the velocity of reaction is the rate of passage of the sulphur dioxide through a layer of sulphur trioxide, absorbed at the surface of the platinum. From this point of view, what is measured is a diffusion velocity, not a reaction velocity, for it is supposed that the sulphur dioxide and the oxygen, when they have reached the platinum, react with great rapidity. Bodenstein has further shown that the rate of union of the two gases under the influence of other catalysts is governed by the same factors. Not only so, but it has been found that the rate of change in many other heterogeneous catalytic reactions is, in all probability, determined by the physical process of diffusion. This is the case with the union of hydrogen and oxygen in contact with heated porous porcelain (*see* Bone and Wheeler, Phil. Trans. 1906, 206, 1); in this instance, the rate of union of the gases appears to be determined to a large extent by the rate of occlusion of hydrogen.

Additional support to the view that the velocity of a heterogeneous catalytic reaction may be determined mainly by a diffusion process, is furnished by the relatively low value of the temperature coefficient in these cases. As already indicated, the velocity of a homogeneous chemical reaction is doubled or trebled for every rise of 10°, but the value of $\frac{k_{T+10}}{k_T}$ for a heterogeneous reaction is frequently not much greater than the value (about 1·3) we should expect if the rate of reaction were determined by a diffusion velocity alone.

Among the most important catalytic reactions are those which take place under the influence of enzymes. These catalysts are able to promote changes in organic matter which, in their absence, can be effected only with great difficulty. There is a close analogy between enzymes and ordinary inorganic catalysts, but it is frequently found that, owing to the operation of various factors, the course of a reaction which takes place under the influence of an

enzyme, deviates considerably from what we should expect on the basis of the law of mass action. In the inversion of sucrose by invertase, for example, the velocity coefficient, calculated by the formula for a unimolecular reaction, increases with the time (Brown, Chem. Soc. Trans. 1902, 81, 373). This is shown by the following table, which refers to the inversion of a 9·48 p.c. sucrose solution at 30°; the symbol x stands for the fraction of the total sucrose inverted by time t:—

t min.	x	$\frac{1}{t}\log\frac{1}{1-x}$
30	0·265	0·00445
64	0·509	0·00483
120	0·794	0·00571
180	0·945	0·00698
240	0·983	0·00737

The departure from the law of mass action becomes still clearer when experiments are made in which a constant amount of invertase is allowed to act for a given time on varying amounts of sucrose in a constant volume of solution. Such experiments show that the enzyme, instead of inverting a *constant fraction*, as required by the law of mass action, has inverted a *constant weight* of sucrose in the given time; only when the quantity of sucrose is very small is the law of mass action obeyed (*see* p. 749). In the hydrolysis of starch by diastase, and of milk sugar by lactase, it is similarly found that the amount of change induced by the enzyme is, for the initial portion of the change, a linear function of the time (*see* Brown and Glendinning, Chem. Soc. Trans. 1902, 81, 388; E. F. Armstrong, Proc. Roy. Soc. 1904, 73, 500); the later portion of the change, when the amount of catalyst is larger relatively to the amount of carbohydrate, conforms to the law of mass action.

Another peculiarity about enzyme action, which is frequently observed, is that the activity of the enzyme does not remain constant throughout the whole course of the change which it induces. In the hydrolysis of amygdalin by emulsin, and of milk sugar by lactase, the products of reaction seem to exert a specific influence in putting the enzyme out of action (*see* Tammann, Zeitsch. physikal. Chem. 1892, 16, 271; Armstrong, Proc. Roy. Soc. 1904, 73, 500). This is indicated by the regular falling off in the value of $\frac{1}{t}\log\frac{1}{1-x}$ as the reaction proceeds, that is, as the products of the reaction accumulate.

Mechanism of catalysis.—Many theories have been advanced as to the way in which a catalyst exerts its influence. According to one very commonly accepted view, a catalyst is effective because it combines with the substrate, and this intermediate compound then breaks up into the final products of change, the catalyst being liberated. Obviously, if this account of catalytic change is to give an adequate interpretation of the phenomena, it must be supposed that the formation and decomposition of the intermediate compound together require a shorter time for their occurrence than the direct change itself. There is a good deal of evidence, largely of an indirect kind, in favour of the view that combination takes place between catalyst and substrate. The increased stability of invertase in presence of sucrose, the specificity of enzymes, and the occurrence of a linear portion in the time curve for the hydrolysis of sugars, are facts which contribute to this evidence. In the case of the catalytic influence of molybdic acid on the reaction between hydrogen peroxide and hydrogen iodide, it has been definitely shown that combination takes place between the molybdic acid and the hydrogen peroxide. Aluminium chloride also, well known as a catalytic agent, forms definite compounds with the substances the reactivity of which it promotes. But although we may frequently assume the very probable formation of intermediate compounds in enzyme action and catalysis generally, it is quite impossible, in many cases, to specify the nature of these compounds.

There are, moreover, many cases in which the efficiency of a catalyst depends almost certainly on something else than the formation of intermediate compounds. The investigation of non-homogeneous catalytic reactions, such as the combination of sulphur dioxide and oxygen under the influence of platinum, or the union of hydrogen and oxygen under the influence of porous porcelain, has led to the conviction that in these cases occlusion or adsorption of the reacting substances occurs at the surface of the catalyst, and that the higher concentration of the reagents thus secured is responsible for the greater velocity of reaction. It is possible to interpret enzyme action also on this basis, for the solution of an enzyme is, strictly speaking, a non-homogeneous system.

Bibliography. — Chemical Statics and Dynamics, J. W. Mellor; Thermodynamics of Technical Gas Reactions, F. Haber; Nature of Enzyme Action, W. M. Bayliss; Catalysis and its Applications, Conroy (J. Soc. Chem. Ind. 1902, 21, 302). J. C. P.

CHERRY. The fruit of *Prunus avium* (sweet cherry) or *P. cerasus* (Morella cherry). There are many varieties. König gives, as the composition of ordinary cherries:

Water	Protein	Free acid	Invert sugar	Saccharose	Other carbohydrates	Fibre	Ash
80·6	1·2	0·7	8·9	0·5	1·8	5·8	0·5

Included in the carbohydrates is 0·6–1·0 p.c. of pentosans (Wittreaun, 1901). A more detailed examination by Keim (Zeitsch. anal. Chem. 1891, 30, 401) showed that in the unripe fruit of *P. cerasus*, citric, malic, and succinic acids were present; that cane sugar was present, but diminished greatly as the fruit ripened. The ripe fruit contained no succinic acid, but malic and citric acid equal to 0·46 p.c. expressed as malic acid, were present, and the sugars were dextrose, levulose, and traces of inositol. Shaw (Expt. Station Record, 1899) found, as the mean of the analyses of 13 varieties of cherries:

Average weight	Whole fruit		Flesh		In the flesh			
	Flesh	Stone	Juice	Residue	Water	Protein	Sugar	Ash
5·29 grams	93·9	6·1	86·4	13·6	81·3	0·9	11·2	0·5

König gives, as the mean of many analyses of cherry juice: Sp.gr. 1·0737; total solids, 19·4; sugar, 12·8; protein, 0·42; free acid, 0·75; tannin, 0·09; ash, 0·55, grammes per 100 c.c.

König gives, as the composition of the ash:

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl	Mn_3O_4
Whole fruit .	54·8	4·4	5·8	5·4	1·5	15·6	5·4	5·0	1·6	8·0
Flesh only	50·1	—	7·0	5·2	—	12·9	—	—	—	—

The kernels of cherry stones contain:

Water	Protein	Fat	Nitrogen-free extract	Fibre	Ash
41·0	6·9	14·1	33·4	3·5	1·0

The kernels contain about 0·82 p.c. of amygdalin.

Dried cherries contain, according to analyses by König and Krauch (flesh only):

Water	Invert sugar	Other carbohydrates	Protein	Fat	Fibre	Ash
49·9	31·2	14·3	2·1	0·3	0·6	1·6

H. I.

CHERRY BARK TANNIN *v.* TANNINS.

CHERRY LAUREL OIL *v.* OILS, ESSENTIAL.

CHERRY TREE GUM *v.* GUMS.

CHERT. (*Feuerstein, Hornstein,* Ger.) A siliceous mineral allied to chalcedony and flint. Similar terms are applied to hornstone and to any impure flinty rock, including the jaspers. It is worked extensively from carboniferous limestone quarries in Flintshire, especially at Halkin and Talacre in Denbighshire, Derbyshire, and at Reeth in Yorkshire. It is used in potteries for paving the mills in which flints are ground. The following is an analysis of a sample from Vizzin, Sicily, given by Ricciardi (Gazz. chim. ital. 11, 319):—

Interior

SiO_2	Al_2O_3	FeO	CaO	H_2O	Sp.gr. at 22°
96·31	0·30	0·25	0·47	2·81=100·14	2·572

White crust metamorphosed by heat

SiO_2	Al_2O_3	FeO	CaO	H_2O	Sp.gr. at 22°
97·02	0·32	3·39	0·55	1·68=102·96	2·520

CHESSYLITE or **CHESSY COPPER.** (*Kupferlasur,* Ger.) A blue oxycarbonate of copper, $2CuCO_3{\cdot}Cu(OH)_2$, found native at Chessy near Lyons (*v.* COPPER).

CHESTNUT. The sweet chestnut is the seed of *Castanea vesca,* the horse-chestnut that of *Æsculus hippocastanum.*

Average composition:

	Water	Protein	Fat	Carbohydrates	Fibre	Ash
Sweet chestnuts:						
Fresh kernels .	38·5	6·9	8.0	44·9		1·7
Dried kernels .	5·8	10·6	10·0	70·9		2·7
Spanish . .	10·0	9·3	7·5	68·1	2·4	2·7
Horse chestnuts	38·9	4·8	4·6	46·2	3·7	1·8
,, (air-dried)	14·8	6·8	5·1	68·3	2·7	2·2

Sweet chestnuts are largely used as human food; the horse-chestnut has been tried as cattle food, with success (Gay, Ann. Agron. 1896, 22, 401).

The kernels of an aquatic plant, *Trapa bispinosa,* are extensively used as food under the name of water-chestnut, in the North West Provinces of India, being roasted and pounded to a flour. Hooper (Pharm. J. Trans. 1894, 53, 22) found this flour to contain:

Water	Protein	Fat	Sugar and gum	Starch	Cellulose	Ash
4·2	8·4	1·0	14·4	63·8	3·6	4·7

The ash of the flour contained a little manganese, which, however, was abundant in other parts of the plant.

The bark of the horse-chestnut, especially in early spring, contains *æsculin* $C_{15}H_{16}O_9$, the glucoside of æsculetin $C_9H_6O_4$. Another glucoside, *argyræscin* $C_{27}H_{42}O_{12}$, occurs in the seeds of the horse-chestnut (Rochleder, J. pr. Chem. 1862, 87, 1).

Sweet chestnuts contain small quantities of resins and tannin, and included in the carbohydrates are sugar, dextrin, starch, and other substances. Very diverse amounts of these have been found by different observers. In the horse-chestnut, according to Laves (Zeitsch angew. Chem. 1902, 1013), there are about 50 p.c. starch, 14 p.c. cane sugar, 13 p.c. glucose, and 0·2 p.c. tannin. H. I.

CHESTNUT EXTRACT. The wood of the Spanish chestnut, *Castanea vesca,* though it contains only 3–6 p.c. of tannin, is the source of the much-valued chestnut extract. The bark contains more tannin than the wood (17 p.c.), but is not much used. The tree, which grows to from 60 to 80 feet in height, is abundant in Italy, the South of France, and Corsica, where it forms immense forests, and it is also very common in America.

Trimble (The Tannins), who very carefully examined the tannin, obtained analytical data and reactions which indicated that it was identical, or nearly so, with gallotannin, but it is probable that this wood also contains traces of a catechol tannin, for a certain quantity of a red-colouring matter is also present, which resembles in character a phlobophane. Some writers have suggested that chestnut tannin is a methyl ether of ordinary gallotannin, but there is apparently no definite evidence in support of this theory.

Chestnut is employed almost entirely in the form of extract, the strength of which varies, but usually contains from 26 to 32 p.c. of tannin. The extract is frequently decolourised, and sometimes mixed with quebracho extract and other materials. Chestnut tannin is the tannin which is most largely employed for the dyeing of silk. *Castanea vesca* appears to be frequently confused with the horse-chestnut, *Æsculus hippocastanum.* The tannin derived from this latter is, however, of little or no practical value.

A. G. P.

END OF THE FIRST VOLUME.

PRINTED IN GREAT BRITAIN BY WILLIAM CLOWES AND SONS, LIMITED, BECCLES.

00039168

Digitized with financial assistance from

H T Parekh FOUNDATION

An Initiative by HDFC

WITH YOU, RIGHT THROUGH

on 15 October, 2018